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BIOLOGICAL ION EXCHANGE FILTERS AS AN ALTERNATIVE TO BIOLOGICAL ACTIVATED CARBON IN DRINKING WATER

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BIOLOGICAL ION EXCHANGE FILTERS AS AN ALTERNATIVE TO BIOLOGICAL ACTIVATED CARBON IN DRINKING WATER

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DEDICATION

To my beloved parents, friends and everyone who digs science

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It was quite a journey. I learned so much and got a chance to meet amazing people. To make it simple, this journey changed my life path and taught me a new one.

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RÉSUMÉ

Enlèvement de la matière organique naturelle (mon) pose un problème pour les utilitaires de la petite eau potable. Échec d'optimiser la suppression du NOM et sa présence dans l'eau affecte le système de l'eau qui provoque la mauvaise qualité esthétique de l'eau avec le compromis de goût et d'odeur. En outre, le problème de santé associé à la présence de NOM dans les résultats de système de distribution de l'eau dans la formation de produits cancérogènes connus comme désinfectant sous-produit (DBP). En outre, le NOM perturbe le processus de traitement de l'eau dans des arrêts comme membrane fouling et une diminution du taux d'oxydation du fer et du manganèse. En ce qui concerne les impacts négatifs précités du NOM, différentes stratégies ont été étudiés et a suggéré de supprimer le NOM des ressources en eau comme la coagulation, membrane, oxydation, adsorption réversible, charbon actif (AC) et l'échange d'ions (IEX).

Parmi ces méthodes, IEX est considéré comme un traitement alternatif pour supprimer la couleur, SPD et réduire la demande en chlore car il est robuste et facile à utiliser. Cependant, l'inconvénient de filtration IEX est qu'il nécessite une infrastructure permettant de gérer la production de saumure et disposition pour rétablir la capacité de la résine par la régénération. En outre, les résines anioniques servent un environnement propice à la prolifération de la biomasse en absence de régénération, qu'il prévoit la situation pour IEX d'effectuer en mode biologique (BIEX).

Considérant les avantages et les inconvénients de ces méthodes conventionnelles, l'objectif de cette étude est d'étudier l'impact de la promotion de l'activité biologique sur résines comme un coefficient d'absorption pour le NOM et d'évaluer le rendement de BIEX au pilote. Également, comme la nitrification est un processus biologique, étudient la possibilité d'enlèvement de NH3 par échange d'ions biologique pourrait accroître la valeur de l'étude actuelle.

Dans la présente étude, les performances des filtres BIEX a été suivie en parallèle aux filtres GAC, BAC et IEX pendant 442 jours commençant le 28 février 2017. Les colonnes de flux descendant échelle pilote sont trouvaient à Pont-Viau eau potable traitement plante (DWTP). Les colonnes avec 2 mètres de hauteur ont été remplie à moitié avec les médias et exploité avec un débit de 2 m/h. La source d'eau transportent directement depuis Les Priraies rivière aux filtres fournit une situation réelle dans laquelle il a subi les changements saisonniers et fluctuation de turbidité pendant 442 jours. Ports de prélèvement d'échantillons liquides et solides ont été intégrées à un niveau égal au sein de chaque profondeur de la colonne (5, 15, 30, 50, 60, 90 et 100 cm

correspondant à 0,15, 4.5, 9, 15, 18, 27 et 30 minutes de temps de Contact des lit vide (EBCT)). Pour étroitement et précisément contrôler l'état opérationnel et évaluer les performances des filtres en ce qui concerne la suppression du NOM et de la nitrification, des colonnes effluents et eaux de source ont été échantillonnés par semaine ainsi que de l'échantillonnage des médias au sein de 5 cm de profondeur des médias à surveiller capacité de la résine et l'activité biologique. Afin d'étudier la cinétique de colonnes, les profil échantillonnage a été effectué au sein de la profondeur de médias de colonnes en avril, juillet, novembre et après régénération BIEX en janvier. Après régénération colonne BIEX jour 331, expérience continue à observer la performance BIEX pendant 111 jours (15 mai 2018).

Les résultats ont montré des changements de mode de BIEX tout au long de l'année de IEX mode à fonctionnant en mode épuisement IEX, puis transfert vers un mode biologique à chaud (> 15 ºC) et froid (< 15 °C) température. Pour les 64 premiers jours de fonctionnement, la colonne BIEX gardé DOC sous l'objectif de traitement (≈1.4 mg/L, élimination de DOC de 80 %). BIEX atteint à percée DOC après 92 jours d'opération (15.5ºC) sans régénération qui a conduit à une élimination de DOC ≈76 % plutôt qu'à 80 % par le biais de hebdomadaire régénéré IEX comme un% ≈2 enlèvement de DOC par BAC. Épuisement de la résine toute de la colonne BIEX simultanée à la percée de BIEX DOC indique la fonction BIEX altérant le mode biologique. BIEX gardé d'exploitation pour les prochains jours 240 sans régénération et enlevé ≈51 % DOC en mode biologique comparé à ≈ 8 % de BAC. Après la régénération BIEX sur 23 janvier 2018, le filtre BIEX commence à effectuer tout aussi au filtre IEX en supprimant le NOM puis le même modèle que le début du projet. Correspondant à la suppression de la DOC, BIEX gardé la possibilité de formation de DBP aussi bas que l'objectif de traitement standard pour les deux premiers mois de l'opération. La formation de DBP augmentait avec la percée de la DOC, puis a diminué sous l'objectif de traitement pendant le mode de la biodégradation de BIEX à haute température. Après 50 jours d'opération BIEX, ainsi que l'augmentation de la température de l'eau (> 7ºC) et croissance de biofilm sur des billes de résine, BIEX commence à éliminer l'ammoniac (retrait de ≈43 %). Jour 78 de l'opération (11.3ºC), BIEX enlevé AMMONIAC presque égal au filtre du BAC (72,24 % contre enlèvement 74,90 % respectivement). BIEX atteint la suppression totale du NH3 (100 %) le jour 162 (22.8ºC) par rapport à 98,5 % d'enlèvement par BAC.

BIEX est régénéré avec succès après 331 jours de fonctionnement. Le filtre BIEX récupéré

capacite d'Echange ionique, optimale retrait de NOM de la même façon pour le filtre IEX (inférieures à 2 mg/L) par la suite et puis a suivi le même schéma d'élimination comme le début du projet. Le filtre BIEX n'a pas obtenu l'enlèvement de l'ammoniac tout de suite après la régénération. Finalement, comme pour le début du projet, BIEX commencé nitrification et atteint impressionnante nitrification (≈ 98%) 109 jours après la régénération BIEX (12.4ºC). Dans l'ensemble, les résultats après 111 jours de régénération BIEX manifestent que le filtre BIEX suivi modèle de performance similaire pour d'autres facteurs aussi bien.

ABSTRACT

Natural organic matter (NOM) removal poses a challenge to small drinking water utilities. Failure to optimize the removal of NOM and its presence in water affects the water system, thereby causing poor aesthetic quality of water with compromised taste and odor. In addition, a health concern associated with the presence of NOM in water distribution systems is the formation of carcinogenic products known as disinfectant by-products (DBPs). Besides, NOM disrupts the process of water treatment in cases such as membrane fouling and a decrease in the oxidation rate of iron and manganese. Considering the aforementioned adverse impacts of NOM, different strategies have been studied and suggested to remove NOM from water resources such as coagulation, membrane filtration, oxidation, reversible adsorption, activated carbon (AC) filtration, and ion exchange (IEX).

Among these methods, IEX is considered an alternative treatment to remove color and DBPs and to reduce the chlorine demand, as it is robust and easy to operate. However, the drawback of IEX filtration is that it requires an infrastructure to manage brine production and disposal to restore resin capacity through regeneration. Furthermore, anionic resins serve as a favorable environment for biomass proliferation in the absence of regeneration, which provides suitable conditions for IEX to perform in the biological mode (BIEX).

Considering the advantages and disadvantages of these conventional methods, the objective of this study is to investigate the impact of promoting biological activity on resins as a removal factor for NOM and to assess the BIEX performance at a pilot scale. Additionally, as nitrification is a biological process, investigating the possibility of NH_3 removal by BIEX could enhance the current study's value.

In the current study, the BIEX filter performance was monitored in parallel to GAC, BAC, and IEX filters for 442 days starting from February 28, 2017. The down-flow pilot-scale columns were located at the Pont-Viau Drinking Water Treatment Plant (DWTP). The columns with 2 m height were half-filled with media and operated at a 2 m/h flow rate. The source water transported directly from the Les Prairies River to the filters provided an actual situation in which it underwent seasonal changes and turbidity fluctuation during the 442 days. Liquid and solid sampling ports were embedded at equal levels within each column depth (5, 15, 30, 50, 60, 90, and 100 cm corresponding to 0.15, 4.5, 9, 15, 18, 27, and 30 min Empty Bed Contact Time (EBCT)). To closely

and precisely control the operational condition and evaluate the performances of the filters for NOM removal and nitrification, the columns' effluents and source water were sampled weekly along with sampling media within 5 cm depth of the media to monitor resin capacity and biological activity. To study the kinetics of columns, profile sampling was performed within the media depth of the columns in April, July, November, and after BIEX regeneration in January. After regenerating the BIEX column on day 331, the experiment was continued to observe the BIEX performance for 111 days (until May 15, 2018).

The results showed changes in the BIEX mode throughout the year from operating in the IEX mode to the IEX exhaustion mode and then to a biological mode in warm (> 15°C) and cold (< 15°C) temperatures. For the first 64 days of operation, the BIEX column kept the DOC below the treatment objective (≈1.4 mg/L, 80% DOC removal). BIEX reached the DOC breakthrough after 92 days of operation (15.5°C) without regeneration, which led to ≈76% DOC removal rather than ≈80% through weekly regeneration of IEX as well as ≈2% DOC removal through BAC. The complete resin exhaustion of the BIEX column concurrent to the BIEX DOC breakthrough indicates the change in BIEX function to the biological mode. BIEX continued operation for the next 240 days without regeneration and removed ≈51% DOC in the biological mode compared to ≈8% by BAC. After BIEX regeneration on January 23, 2018, the performance of the BIEX filter became equivalent to that of the IEX filter for NOM removal and followed the same pattern as that in the beginning of the project. Further, BIEX reduced the potential of DBP formation and kept it as low as the standard treatment objective for the first two months of operation. The DBP formation increased with DOC breakthrough and then decreased below the treatment objective during the biodegradation mode of BIEX at a high temperature. After 50 days of BIEX operation, along with an increase in water temperature (>7°C) and biofilm growth on the resin beads, BIEX started to remove ammonia (≈43% removal). On day 78 of the operation (11.3°C), BIEX removed ammonia nearly equal to that removed by the BAC filter (72.24% vs. 74.90% removal, respectively). BIEX completely removed NH_3 (100%) on day 162 (22.8°C) compared to 98.5% removal by BAC.

BIEX was regenerated successfully after 331 days of operation. The BIEX filter recovered the IEX capacity, optimally removing NOM similar to the IEX filter (below 2 mg/L) afterward, and then followed the same removal pattern as that in the start of the project. The BIEX filter failed to achieve ammonia removal right after the regeneration. Eventually, similar to the beginning of the

project, BIEX started nitrification and achieved impressive nitrification (≈98%) 109 days after the BIEX regeneration (12.4°C). Overall, the results after 111 days of BIEX regeneration showed that the BIEX filter followed a similar performance pattern for other factors as well.

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LIST OF SYMBOLS AND ABBREVIATIONS

AC	Activated carbon
AE	Activation energy
AEC	Anion exchange capacity
AOB	Ammonia-oxidizing bacteria
AOP	Advanced oxidation process
ATP	Adenosine triphosphate
BAC	Biological activated carbon
BDOC	Biodegradable dissolved organic carbon
BIEX	Biological ion exchange
BOM	Biodegradable organic matter
BV	Bed volume
CDWQG	Canadian drinking water guideline
CFR	Co-flow regeneration
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DWTP	Drinking water treatment plant
EBCT	Empty ced contact time
EDTA	Athylenediaminetetraacetic acid
EPS	Axtracellular polymeric substance
ES	Effective size
FA	Fulvic acid
GAC	Granular activated carbon
HA	Humic acid
HAA	Haloacetic acid
HIA	Hydrophilic acid
HIB	Hydrophilic base
HIN	Hydrophilic neutral
HMM	High molar mass
HMW	High-molecular-weight
HOA	Hydrophobic acid

HOB	Hydrophobic base
HON	Hydrophobic neutral
HPC	Heterotrophic plate count
HPLC	High-performance liquid chromatography
IC	Ion chromatography
IEX/ IX	Ion exchange
IMM	Intermediate molar mass
LC-OCD	Liquid chromatography - organic carbon detection
LC-OND	Liquid chromatography of organic nitrogen detection
LMM	Low molar mass
LMW	Low-molecular-weight
MF	Microfiltration
MIEX	Magnetic ion exchange
MTZ	Mass transfer zone
NBDOC	Non-biodegradable compounds
NF	Nanofiltration
NOM	Natural organic matter
NTU	Nephelometric turbidity unit
PAU	Potential acetate uptake
PGR	Potential glucose respiration
PZG	Plane of zero gradient
RFR	Reverse-flow regeneration
RO	Reverse osmosis
SSF	Slow sand filtration
SUVA	Specific ultra-violet absorbance
THM	Trihalomethane
TOC	Total organic carbon
UF	Ultrafiltration
UFC	Uniform formation condition
US EPA	United states environmental protection agency
UVA	Ultra-violet absorbance

WHO World health organization

WTP Water treatment plant

LIST OF APPENDICES

CHAPTER 1 INTRODUCTION

1.1. Background

Natural organic matter (NOM) refers to a series of chemical compounds originating from animals, plants, and microorganisms after they are transformed into particulate and dissolved organic carbon (Aiken and Cotsaris, 1995; Hong and Elimelech, 1997). NOM is present in most drinking water resources as proteins, polysaccharides, humic acids, fulvic acids, and amino acids. The NOM present in water may be from internal sources (autochthonous) or external sources (allochthonous). Allochthonous NOM arises from the transfer of land-based NOM to water by rainfall or drainage (Aiken and Cotsaris, 1995; Hong and Elimelech, 1997) while allocthonous NOM is produced in the aquatic environment (e.g., by algae growth). Depending on the characteristics of the watershed and seasonal changes, the concentrations and characteristics of NOM from external and internal sources vary.

In addition to the aesthetic issues and disruptions in water treatment and distribution caused by the presence of NOM in water, NOM reacts with the chlorine added to water in the final disinfection step. This reaction produces chemical compounds known as disinfectant byproducts (DBP), which have potential adverse impacts on human health (Kleiser and Frimmel, 2000; Singer, 2006) (Xie, 2003). NOM is not regulated by Canadian drinking water guidelines (CDWQG), the United States Environmental Protection Agency (US EPA), or the World Health Organization (WHO). Because of health concerns arising from DBP formation, NOM concentration reduction has been suggested before chlorination. In Canada, the objective is to limit trihalomethane (THM) and haloacetic acid (HAA) concentrations to <100 µg/L and <80 µg/L, respectively. The Quebec Drinking Water Quality Standards stipulate even lower limits of 80 µg/L and 60 µg/L, respectively, as measured using a running average of trimestral worst-case samples collected from a distribution system. WHO guidelines regulate THM contents using separate values for chloroform (0.3 mg/L), bromoform (0.1 mg/L), dibromochloromethane (0.1 mg/L), and bromodichloromethane (0.06 mg/L).

To avoid exceeding DBP regulations, NOM is typically removed from drinking water via methods including coagulation, membrane filtering, oxidation processes, activated carbon (AC) adsorption,

or ion exchange (IEX), among which IEX has a particularly good cost performance metric. The IEX process is defined based on the exchange of ions between resin beads and contaminants. Among varying types of resin, anion exchange using negatively charged compounds can remove NOM. Upon successive investigations of resins for NOM removal, macroporous strong-base polyacrylic-structured Purolite A860™ resin demonstrated the best total organic carbon (TOC) removal of 93% and highest regeneration efficiency compared to other alternatives (Bazri, 2016; Bazri et al., 2016). However, the necessity of frequent regeneration complicates this method because of the required disposal of spent brine, which negatively impacts the environment.

IEX resins are typically regenerated every two to three days. Earlier work from our group in RES'EAU WaterNet has shown that operating IEX filters without regeneration allowed maintenance of long-term (one-year) NOM removal. The study reported herein was conducted at the laboratory scale with 0.45-µm pre-filtered surface water (Schulz et al., 2017; Winter et al., 2018). To further investigate this mode of operation on natural surface water, four columns including granular activated carbon (GAC), biological activated carbon (BAC), IEX, and biological IEX (BIEX) filters were set up in parallel and operated for a period of >1 year at the Pont-Viau water treatment plant (WTP). These four filters were fed directly with Des Prairies River water without pretreatment. Routine influent/effluent water quality assessments and solid media characterizations were performed to gain a better understanding of the differences of the filter media (BAC vs. resin) and operation modes (with and without regeneration) on the process performance. This thesis reports the results of this investigation, which confirmed that the BIEX mode of operation offers significant advantages over the traditional mode of operation of IEX while also providing significantly better performance than BAC and GAC filtering.

1.2. Research objectives and hypothesis

The idea of IEX in the biological mode was introduced at the University of British Columbia (Winter et al., 2016). They studied the performance of BIEX in comparison to IEX (Purolite A860) using 0.45-µm pre-filtered water, diluted with tap water to a constant dissolved organic carbon (DOC) concentration of 5 mg/L. They operated their lab-scale systems for two continuous months at room temperature (22°C), with the columns backwashed and regenerated monthly via three methods of regeneration (see section 2.3.5). Unlike previous studies, this experiment used natural surface water and thus considered natural changes in the water resource characteristics and

seasonal temperature changes.

The general objective of the current project was to confirm the viability of BIEX filter operation for NOM removal in direct feeding by colored and turbid surface water. A BIEX column was therefore operated for more than one year in parallel to an IEX column (regenerated weekly), as well as GAC and BAC columns. The specific objectives were:

1. Compare different media for NOM removal (resins vs. AC)
2. Assess operation modes in BIEX media
3. Test potential nitrification on BIEX media
4. Confirm the feasibility of regenerating BIEX media after long-term operation
5. Evaluate the effects of temperature and turbidity on BIEX performance
6. Measure biofilm colonization on the various media

Table 1.1 summarizes the various research hypothesis evaluated in this project, as well as the experimental approaches used to test them.

Table 1.1: Hypotheses and related experimental approaches

Phase	#	Hypotheses	Experimental approach	Expected results
Removal Efficiency	1	Under biological mode, BIEX filtration allows for a higher NOM removal than BAC filtration.	Pilot-scale: Running 4 columns in parallel (IEX, BIEX, GAC & BAC), monitoring and studying parameters weekly and monthly (section 3.1).	After IX exhaustion, BIEX maintains a statistically significant lower TOC concentration than a BAC filter operated under identical conditions.
	2	A colonized BIEX filter can fully remove ammonia in warm waters similarly to BAC filter.		BIEX removes ammonia as well as BAC in biodegradation mode.
Mechanism Investigation	3	Temperature has a lower impact on BIEX performance than BAC.		Temperature impact (assessed through calculated energy of activation) is higher for BAC filtration than for BIEX.
	4	BIEX ion exchange capacity can be restored after one year of operation with a regular brine regeneration.	BIEX filter regeneration after one year with the same method as the one used to regenerate IEX filter weekly.	After regeneration, resin capacity is equivalent to the control IEX reactor. Performance of BIEX after regeneration is equivalent to the IEX filter.

1.3. Structure of thesis

This thesis is divided into six chapters as follows:

- Chapter 1: An overview on the background of the current study and its research objectives/hypothesis;
- Chapter 2: A literature review on NOM characteristics and concerns, information on conventional NOM removal methods, and discussion of removal mechanisms;
- Chapter 3: The experimental plan and detailed methodology;
- Chapter 4: An article published in the *Journal of Water Research*, titled "Long-Term Performance of Biological Ion Exchange for the Removal of Ammonia and Natural Organic Matter from Surface Waters before regeneration;"
- Chapter 5: The results for the remaining parameters, before and after regeneration of BIEX;
- Chapter 6: General conclusions and recommendations for future studies.

CHAPTER 2 LITERATURE REVIEW

2.1. Natural organic matter

NOM is primarily composed of carbon (~50%), oxygen (~40%), and hydrogen (~4%), with minor heteroatom constituents (~2%) including nitrogen, sulfur, and phosphorus (Hertkorn et al., 2008). It originates from plants, animals, and microorganisms, which are biodegraded and altered into particulate organic carbon and DOC (Aiken and Cotsaris, 1995; Hong and Elimelech, 1997). NOM is present in almost all drinking water resources at various concentrations depending on the source of NOM (Matilainen and Sillanpaa, 2010; Pelekani and Snoeyink, 1999).

2.1.1. NOM characteristics

NOM characteristics depend on its origin, which is usually the degradation of plants, animals, and microorganisms (Pelekani and Snoeyink, 1999). NOM sources are typically classified as allochthonous or autochthonous. Allochthonous organic compounds are decayed vegetation transported from the watershed to the water body, streams, or groundwater flow via rainfall or drainage (Aiken and Cotsaris, 1995). Allochthonous compounds are higher in carbon content than autochthonous compounds, so allochthonous NOM is more prevalent in water sources with higher TOC (Ruttner, 1963). The quantities of externally and internally sourced NOM depend on the watershed characteristics of a water body. Allochthonous NOM is typically found in lakes with large volumes of water flowing through them, like river lakes and mountain lakes (Ruttner, 1963). Drainage from areas with trapped decaying vegetation, such as bogs and swamps, provides significant humic substances. These humic substances can either be released directly into a water body as dissolved NOM or be transported as particles (Kornegay et al., 2000). Meanwhile, autochthonous compounds are usually found in rivers with low surface runoff influx (Ruttner, 1963). Drainage from soils rich in mineralized compounds contains small amounts of carbon, which indicate high quantities of autochthonous organic matter (Kornegay et al., 2000). In addition, because the occurrence of autochthonous compounds is due to the activity of algae, bacteria, and macrophytes (photosynthetic activity) (Ruttner, 1963), the presence of waterborne nutrients (nitrogen and phosphorous) and the water temperature are important in the formation of autochthonous organic matter (Kornegay et al., 2000).

As reported by Thurman (1985), almost 95% of organic matter is dissolved in water, including

both aquatic humic and non-humic substances. About 50% of DOC consists of aquatic humic substances (40% fulvic acid (FA) and 10% humic acid (HA)), while the remaining 50% consists of non-humic substances, such as 30% hydrophilic acid, 10% carbohydrates, <8% carboxylic acids, <3% amino acids, and <1% hydrocarbons.

Humic substances have higher molecular weights than non-humic substances (Edzwald, 2011). Among humic substances, humic acids have molecular weights two to ten times higher than fulvic acids; they also have higher aromatic contents, inducing lower solubility relative to fulvic acids (Vik and Eikebrokk, 1989). Because of the lower molecular weights of non-humic substances, their formation processes, and sources, non-humic substances are considered the major biodegradable fraction of NOM (Kornegay et al., 2000). Various studies on the biodegradability of humic substances indicate that they are the sole carbon source for biofilm growth in distribution systems. Other studies have indicated poor biodegradability of humic substances in experimental conditions (Prévost et al., 2005).

NOM can also be categorized based on its hydrophobicity, which is correlated with the aromatic structures of the fractions of hydrophobic acids (HOA), hydrophobic bases (HOB), hydrophobic neutrals (HON), hydrophilic acids (HIA), hydrophilic bases (HIB), and hydrophilic neutrals (HIN) (Table 2.1).

Table 2.1: NOM fraction and characteristics

	NOM	Structure	MW (Da)[1]	Hydrophobicity	Biodegradibility[2]	Details
Non-humic Substances	**Tannins**	Aromatic	500-3000	Weak hydrophobic acid	Biodegradable	Originated from decaying vegetation and leaves negatively charge at neutral pH
	Phenols	Aromatic	N/A	Weak hydrophobic acid	Biodegradable	Negatively charge at neutral pH
	Hydrocarbons	Aliphatic	100-70,000	Hydrophobic neutral	Biodegradable	Typically negligible in most waters
	Sugars	Aliphatic	N/A	Hydrophilic acid	Biodegradable	Originated from structural components of microorganisms cell wall[3]
	Polysaccharides	Aliphatic	120-900	Hydrophilic neutral	Biodegradable	Originated from algal by-products, Microorganisms constituents [4]
	Proteins	Aliphatic	250-850	Hydrophobic base	Biodegradable	N/A

[1] (CBCL-Limited., 2011)
[2] *(Kornegay et al., 2000; Prévost et al., 2005)*
[3] (Biber et al., 1996)
[4] (Edzwald, 2011)

Table 2.1: NOM fraction and characteristics (continued)

	NOM	Structure	MW (Da)[1]	Hydrophobicity	Biodegradibility[2]	Details
Non-humic Substances	**Amino Acids**	Aromatic/ aliphatic	75-205	Hydrophilic base	Readily biodegradable	N/A
	Fatty Acids	Aliphatic	250-850	Hydrophilic polar head group/ Hydophobic alphitic tail	Biodegradable	N/A
Aquatic Humic Substances	**Humic Acids**	HAs are more aromatic than FAs	1000s	Hydrophobic Acid#	Difficulty to biodegrade	Negative form at pH range of natural waters
	Fulvic Acids		Several 100s	Hydrophobic Acid#		

[1] (CBCL-Limited., 2011)
[2] (Kornegay et al., 2000; Prévost et al., 2005)

2.1.2. Issues caused by NOM in drinking water

Failure to an optimized NOM removal and its presence in water affects water systems in two manners: deteriorating the drinking water quality and disrupting water treatment processes, with the following possible results:

- Poor aesthetic quality of the water;
- Issues with taste and odors (Christman and Ghassemi, 1966);
- Disinfectant By-Product (DBP) formation (Kleiser and Frimmel, 2000; Xie, 2003);
- Bacterial regrowth and biofilm formation in the water distribution system (Vanderkooij, 1992);
- Adverse effects on the adsorption capacity and oxidation kinetics of micropollutants (Smith and Weber, 1985);
- Potential membrane fouling (Amy and Cho, 1999; Nilson and DiGiano, 1996; Schäfer et al., 2000);
- Negative impact on ultraviolet (UV) light-based advanced oxidation processes (AOPs) (Sarathy et al., 2011);
- Reduced oxidation of iron and manganese (Graveland and Heertjes, 1975).

Because of the negative impacts of NOM in water, NOM elimination is an important goal in drinking water treatment. Different methods have been studied and suggested for NOM removal, as reviewed in the next section (section 0).

2.1.3. Processes for NOM removal from drinking water

Many methods of NOM removal have been studied. Because of the variability of NOM fractions and specific characteristics, most methods can only achieve partial NOM removal (Table 2.2). Listed below are brief descriptions of the most common methods applied for NOM removal in water treatment:

- **Coagulation:**

Coagulation involves the addition of chemicals to destabilize colloids and promote their adherence to each other (Davis and Cornwell, 2013). These hydrolyzing chemicals are usually aluminum salts, iron salts, or organic quaternary amine-based polymers. NOM removal by coagulation

depends on factors including the coagulant type, coagulant dose, NOM characteristics, temperature, pH, and other available ions in the water (Matilainen and Sillanpaa, 2010; Matilainen et al., 2010).

- **Membrane filtration:**

Membrane filtration is a modern water treatment technology based on steric, diffusion, or charge separation mechanisms. The four available membrane types are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Among different membrane types, NF and RO filters can remove NOM (Davis and Cornwell, 2013). However, UF and MF can be used to remove the flocs induced by coagulation agents.

- **Oxidation processes:**

The mechanism of oxidation processing relies on electron transfer from an electron donor to an electron acceptor. Oxidation processes in water treatment for NOM removal include conventional methods, combinations with biological filters, and advanced oxidation processes (AOP). Conventional oxidation, using oxidants such as chlorine, is selective, while AOP converts almost any type of waterborne organic compound, including synthetic organic compounds, to carbon dioxide (Crittenden et al., 2012; Matilainen and Sillanpaa, 2010). Oxidation processes generate oxidation byproducts. The control of oxidations processes in source waters with variable characteristics can be complex.

- **Activated carbon:**

AC, derived by carbonizing natural substances such as wood and coal, is used to remove organic and inorganic matter from water (CBCL-Limited., 2011). It works by an adsorption mechanism. After a few months of operation, AC begins working in a biological mode. This biological activity increases the removal of the biodegradable fraction of NOM (Zearley and Summers, 2012). This method is further discussed in section 2.2.

- **Ion exchange:**

The IEX mechanism consists of the exchange of one ion with another; it is convenient for the removal of charged particles in NOM (CBCL-Limited., 2011; Matilainen, 2007). It is commonly

used in small systems because of its simple operation. Because 60–90% of NOM is charged (Fettig, 1999), the removal rate performance of this process can be high. The main drawback of IEX is the need to regenerate the media every 48–72 h with 80–120 g/L sodium chloride or other regenerants, as described in section 2.3.3; this procedure generates brine waste that may be difficult to dispose because many environmental legislations restrict the release of chlorides to the environment. This method is further discussed in section 2.3.

Table 2.2: Alternative processes for NOM removal

Method	NOM fraction removed[+]	Effectiveness[+]	Drawbacks	Reference
Coagulation	Hydrophobic, mostly HMW	Moderate: ➢ HMM: 94% ➢ IMM: 12-55% ➢ LMM: 3-14%	Depending on the coagulant: ➢ High alkalinity consumption; ➢ Large footprint related to next treatment processes and production of sludge; ➢ Energy intensive.	(CBCL-Limited., 2011)
Membrane (NF & RO)	Depends on the membrane molecular weight cut-off	High: ➢ HMM: 100% ➢ IMM: 52-100%	➢ Membrane fouling; ➢ Complexity of process; ➢ Energy and water intensive; ➢ Expensive; ➢ Pre-treatment is required.	(Matilainen, 2007) (Vickers et al., 1995)
Oxidation Processes	Hydrophobic, mostly LMW	Moderate:	➢ Expensive; ➢ Complexity; ➢ Post-filtration is required to remove transformed NOM, otherwise it would lead to DBP formation.	(CBCL-Limited., 2011)
Activated Carbon	Variable	Moderate: ➢ HMM: 0% ➢ IMM: 30% ➢ LMM: Slightly	➢ Fast exhaustion (=expensive); ➢ Inefficient NOM removal (variable for various NOM fractions); ➢ Variable adsorptive capacity from one GAC to another; ➢ Dependency of adsorptive Nom capacity to other parameter.	(McCreary and Snoeyink, 1980) (CBCL-Limited., 2011)
Ion Exchange	Variable	High	➢ Brine disposal	

[+] (Matilainen, 2007)

2.2. Biological filtration

2.2.1. History of activated carbon vs. other types of media

Filtration is a common process used in most water treatment plants to remove particles, sediments, algae, and various organic and inorganic substances. Particularly for the removal of microorganisms from surface water, filtration is considered important in tandem with chemical disinfection. For this purpose, different types of biological filtration have been practiced, evolving from slow sand filtration (SSF) to BAC (Table 2.3).

The concept of SSF was first proposed in the early 1800s for small communities in Europe. In studies on SSF performance, DOC removal reaching 31% (Collins et al., 1992), AOC removal reaching 40%, and biodegradable organic compound (BDOC) removal reaching 75% have been observed, depending on the temperature and source of the water (Lambert and Graham, 1995). The mechanism of high-molecular-weight (HMW) compound removal by this method is based on adsorption, while for low-molecular-weight (LMW) fractions, adsorption and biodegradation are correlated (de Haan, 1977; Schneider et al., 1984). The performance of SSF is mostly impacted by the biological layer (Schmutzdecke) formed on the top 5 cm of the sand bed. Biodegradation is observed in this layer, as well as ionic reduction (Campos et al., 2002). Regardless of the efficacy of NOM removal by SSF, the slow flow rate of 0.1–0.3 m/h (Campos et al., 2002) limits the applicability of this method for small communities, as it requires a large footprint. In addition, once the Schmutzdecke layer is clogged by particles, it must be physically removed, which introduces a long ripening period necessary to re-establish the biological layer (Davis and Cornwell, 2013).

The need for faster filtration inspired the introduction of rapid filtration, with a flowrate 10 to 50 times higher than that in SSF. The uniformity of the filtering medium with the effective size of 0.34–1.5 mm (Benham and Ross, 2009) in rapid filtration allows the optimization of water passage through the filter (Davis and Cornwell, 2013). Therefore, water can be filtered by the entire bed depth, which reduces the probability of clogging as observed in SSF (Edzwald, 2011). The efficiency of rapid filtration depends on the initial turbidity of water, filter bed configuration, filtration velocity, and filtration run.

To obtain better performance throughout the bed depth, the application of rapid filtration via two media (dual media) was suggested in which the top medium comprises larger particles while the lower medium comprises smaller particles. This arrangement reduces the phenomenon of clogging (Davis and Cornwell, 2013). The top medium is usually a 0.45–0.60-m-thick layer of anthracite or GAC over 0.2–0.3 m of sand (Edzwald, 2011).

The evolution in water treatment practices in the 1980s demonstrated that the adsorption mechanism of GAC filters was progressively converted into biodegradation over long-term operation. GAC provides an environment for heterotrophic bacteria to grow on the media and degrade both organic compounds and micropollutants. All previously mentioned media can potentially establish such conditions for bacteria and biofilm formation, but the irregular shape of GAC facilitates the attachment of bacteria to the surface, especially in cold water conditions (Prévost et al., 2005).

Table 2.3: Evolution of biological filtration

Type of Filtration	Introduced around:	Media effective size (mm)	Layer depth (mm)	Velocity (m/h)	Drawbacks
Slow Sand Filtration	Early 1880s	0.1 - 0.3	0.6 - 1.0	0.1 - 0.3	- Low velocity; - Large footprint; - Only for small communities; - Difficulty in backwashing in case of clogging; - Only for turbidity lower than 10 NTU
Rapid Filtration	Late 1880s	0.34 – 1.5	0.6 -0.76	< 10	- Requires pre- and post-treatment for NOM removal; - high operational cost along requirement of skilled supervision; - Required high energy input; - Requires frequent backwash (every 24-96 hours)*
Dual Media (Anthracite/GAC + Sand)	Mid 1900s	- Anthracite: 0.8 – 2.0 - GAC: 0.8 – 2.0 - Sand : 0.4 – 0.8 **	Top: 0.45 – 0.6 Bottom: 0.2 – 0.3 **	< 15[+]	- Importance of monitoring water quality and excess of skilled operators with increase of flowrate[++]
Biological Activated Carbon	1990s	GAC: 0.8 -2.0	1.8 – 4[O]	5 - 25[O]	No removal of biopolymers[oo]

* (Bruni, 2012)

**(Edzwald, 2011)

[+] (Davis and Cornwell, 2013)

[++](Engelhardt, 2012)

[O](Çeçen and Aktas, 2012)

[oo](Von Gunten et al., 2009)

2.2.2. Biological activated carbon mechanism

BAC filters operate via the two simultaneous removal mechanisms of adsorption and biodegradation. Early in the formation of biofilms on AC, biological activity is limited and the reaction mechanism is simple adsorption via GAC. In this phase, biodegradation is negligible and the removal of organic and inorganic substances is mainly accomplished by adsorption. Later in operation, the adsorption capacity of the GAC is exhausted and biological activity becomes dominant in the removal of contaminants. In this phase, the GAC reactor has changed to the biological mode of operation, typically referred to as BAC (or BGAC).

- **Adsorption:**

Adsorption on AC is defined as the accumulation of substances from the liquid phase on the solid after traversing the interfacial boundary layer (Walter et al., 1972). Adsorption is achieved by two driving forces: the hydrophobicity of the solute and the electrical affinity of the solute for the solid (physisorption and chemisorption). Hydrophilic substances preferentially remain dissolved in solution in the water system, while hydrophobic substances generally become attached to solids (Çeçen and Aktas, 2012). Physisorption arises from weak van der Waals interactions, instead of electron exchange, driving the adsorptive attachment of a substance to a solid surface. The formation of multiple layers is expected in this type of adsorption. At temperatures below 150°C, physisorption is a significant mechanism of adsorption. At lower temperatures and in reversible processes, adsorbates are not strongly attached to the solid surface; in such conditions, physisorption is mostly associated with lower binding energies (Çeçen and Aktas, 2012; Inglezakis and Poulopoulos, 2006). Unlike physisorption, chemisorption occurs by a chemical reaction between the adsorbate and adsorbent; chemical bond formation occurs after electron exchange between the solid surface and the adsorbate. Chemisorption is generally associated with higher binding energies and is more prevalent at higher temperatures, where only monolayer molecular sorption is anticipated (Inglezakis and Poulopoulos, 2006; Walter et al., 1972).

Adsorption is influenced by various factors including the specific surface area and porosity of the AC, solute characteristics, pH, and temperature.

- **Specific surface area of AC:** The specific surface area is defined as the available

surface for adsorption (Çeçen and Aktas, 2012).

- **Porosity of AC:** The number of pores, their physical characteristics, and their distribution influence adsorption. Pores with different sizes affect adsorption in specific manners. Macropores with large widths exhibit the same adsorption mechanism as flat surfaces, while that on mesopores is mainly based on the capillary adsorbate concentration. Meanwhile, all substances of sizes smaller than the pore diameters can be adsorbed on micropores (Dabrowski, 2001).
- **Solute characteristics:** Different properties of the solute impact the adsorption. LMW compounds are more soluble than HMW ones; therefore, HMW compounds are more prone to adsorption by AC. Polarity also affects adsorption; for AC, nonpolar substances are simply adsorbed. The structure and atomic arrangement of the solute affect the adsorption level as well. Longer molecular chains experience greater adsorption, and aromatic compounds are more easily adsorbed than aliphatic compounds.
- **pH:** pH varies depending on two factors: the charges of ions released from organic matter and the acidity of AC. Acidity arises from the functional groups of AC, which are easily released upon exposure to distilled water. In different pH environments, organic molecules possess different charges. Neutral pH typically presents peak NOM adsorption (Karanfil et al., 1999).
- **Temperature:** Liquid adsorption on solid surfaces is affected by temperature. As the temperature is decreased, the adsorption capacity increases, because of the thermodynamics of adsorption reactions (exothermic). Meanwhile, increases in temperature accompany faster solute diffusion into the pores of AC, which may induce faster kinetics (Hassler, 1963).

- **Bioregeneration:**

After a few months of operation, GAC displays another removal mechanism called bioregeneration. Microorganisms have a significant role in bioregeneration, as they revive the adsorptive capacity of the carbon and thus permit further adsorption by AC (Çeçen and Aktas, 2012). Biofilm growth affects the GAC mechanism in the following ways:

- Removal of (slowly) biodegradable substances and non-adsorbable compounds,
- Under shocking loads of toxic organic pollutants, only the outer layer of the

biofilm is affected while the inner layer remains active,

- As the bulk liquid concentration decreases, desorption from carbon particles occurs into the surrounding biofilm or the bulk liquid; desorbed materials may then be biodegraded.
- The substrate within the biofilm moves to carbon until the carbon is saturated, providing sufficient time for slowly biodegradable substances to be biodegraded,
- Transition of GAC reactor to BAC reactor through time (Çeçen and Aktas, 2012).

Different theories for bioregeneration mechanism have been suggested:

- **Bioregeneration by concentration gradient:**

According to this mechanism, biodegradation occurs based on the concentration gradient of organic matter desorbed from the AC surface to the bulk liquid (deJonge et al., 1996; Kim et al., 1997). This can be defined more specifically by the hypothetical line in a biofilm layer called the plane of zero gradient (PZG). This line separates the zone of substances biodegrading in the bulk liquid from the zone of biodegraded substances adsorbed on the AC surface. By the degradation of substances in the bulk liquid and thus the decrease of their concentration, the equilibrium is impaired, driving substrate desorption from the AC and thus inducing AC bioregeneration, which drives the PZG toward bulk liquid (Figure 2.1). Adverse movement of PZG occurs if the concentration increases in the bulk liquid. In this situation, bioregeneration does not happen (Çeçen and Aktas, 2012).

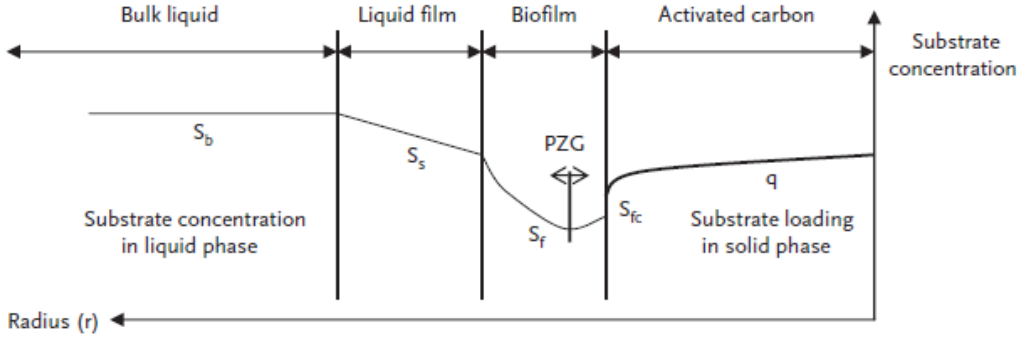

Figure 2.1: Concentration profile of a contaminant during bioregeneration

- **Bioregeneration by exoenzymes:**

According to this theory, bioregeneration occurs by the diffusion of extracellular enzymes excreted by microorganisms into the AC pores and their reaction with adsorbed substances (Kim et al.,

1997; Sirotkin et al., 2001). Different studies have proven the dependency of this mechanism on various factors. Based on these investigations, the adsorption and desorption of extracellular enzymes are prerequisites of bioregeneration Regarding the molecular size of the enzymes, they can only be adsorbed to pores of >10 nm, including macropores and some mesopores. For micropore-adsorbed LMW substances, enzyme adsorption into AC pores is impossible (Martin et al., 2002). In addition, the enzyme penetration of the carbon pores is reduced because of the limited pore size (Klimenko et al., 2002). This mechanism is considered a very slow process because of the slow diffusion of large enzymes into pores. The involvement of exoenzymes in the bioregeneration mechanism requires further investigation (Aktas and Cecen, 2007).

2.2.2.1.Natural organic matter removal

The mechanism for NOM removal is divided into three distinct phases of initial, intermediate, and final. In the initial phase, usually lasting for several months, NOM is removed by adsorption on GAC particles. In this stage, BDOC are adsorbed more than non-biodegradable compounds (NBDOC), favoring the removal of humics, HMW, and LMW depending on the GAC characteristics (Nishijima and Speitel Jr., 2004; Von Gunten et al., 2009).

In the intermediate phase, adsorption and microorganism-induced biodegradation are combined by microorganisms. A decrease in the adsorption of NOM on the AC occurs with the increase of NOM biodegradation. In addition, the biosorption of NOM into the biofilm is observed in this phase; the surface charges of the NOM and biofilm and the NOM molecular size are significant in determining biosorptivity (Çeçen and Aktas, 2012). Because NOM is negatively charged, a negatively charged biofilm obstructs NOM sorption and transport (Carlson and Silverstein, 1998). In this phase, the fraction mainly removed consists of LMW substances because of the biological activity (Von Gunten et al., 2009).

In the final phase, when the GAC adsorption capacity is almost exhausted and the medium begins performing as a biological filter, NOM biodegradation is considered the main mechanism of removal. Therefore, biodegradable fraction and LMW substances are removed in this phase (Çeçen and Aktas, 2012; Von Gunten et al., 2009).

2.2.2.1.1. Kinetics

Different parameters such as temperature, media type, empty bed contact time (EBCT), and pre-oxidation are involved in predicting the removal efficiency of TOC by biological filtration. To simplify the analysis of the impact of these parameters, pseudo-first-order kinetics is often used to model TOC removal (Equation 2.1):

$$C = C_o\,(e^{-k.EBCT}) \qquad \text{(Equation 2.1)}$$

in which C and C_o represent the effluent and influent biodegradable concentrations, respectively, and k is the observed apparent rate constant. The simulated TOC concentration based on Equation 2.1 for different associated k values is represented in Figure 2.2. This shows that TOC concentration by biofiltration does not reach zero because the non-biodegradable fraction of TOC remains, as it is not removable by biofiltration.

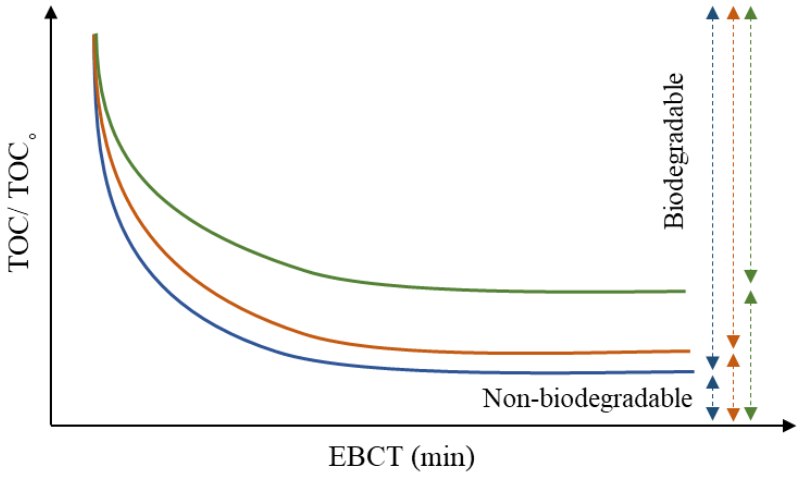

Figure 2.2: Simulated TOC concentration as a function of EBCT for various k values

A recent review on biofiltration performance for TOC removal (Terry and Summers, 2017) showed that increases in temperature in the range 0.5—35°C increase the average TOC removal for non-ozonated and ozonated conditions from 7–10% to 15% and from 11–13% to 20%, respectively. The oxidation condition of water also changes the efficiency of TOC removal; the average is increased from 10% to 15% for ozonated water to non-ozonated water, respectively. In this regard, studies have indicated that the highest TOC removal occurs at temperatures >20°C for ozonated water. The medium type has a minor impact on TOC removal; regardless of other

conditions, the average TOC removal rates are approximately 16%, 14%, and 13% for GAC, sand, and anthracite, respectively. This shows that, regardless of the temperature and oxidation conditions, biofilters remove an average of 12% TOC (minimum of 2%, maximum of 47%) in the EBCT range 2–38 min (average: 12 min).

Terry, and Summers (2017) presented data gathered for TOC removal and *k* constant values under various conditions for ozonated and non-ozonated water (Figure 2.3).

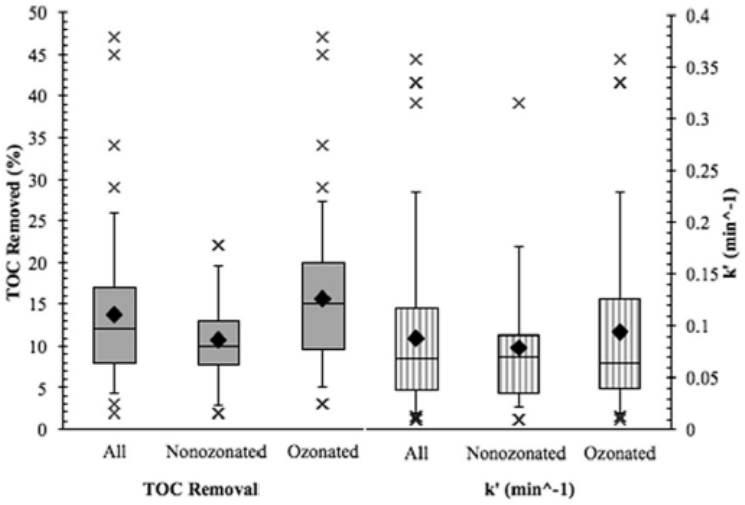

Figure 2.3: Distribution analysis of TOC removal and k constants with and without ozone. The boxes represent 25th, 50th (median) and 75th percentiles, the diamonds represent averages, the error bars represent 5th and 95th percentiles, and the "x" represents outliers (Terry and Summers, 2017)

2.2.2.2.Nitrification

Ammonia is a substance commonly found in water; it can be removed through the biological process called nitrification. The presence of ammonia in water decreases its quality and may promote microorganism growth. Ammonia also increases chlorine demand (Çeçen and Aktas, 2012). Nitrification consists of a two-step oxidation process (section 2.2.2.2.1) of ammonia into nitrite and nitrite into nitrate by aerobic autotrophic bacteria. These bacteria use carbon dioxide as a carbon source, while they obtain energy from the electrons taken from NH_4^+ and NO_2^- by dissolved oxygen, which is either available within the cell or taken from outside the cell (Lájer, 2012; Metcalf & Eddy Inc. et al., 2014). This group of bacteria in charge of nitrification is typically called ammonia-oxidizing bacteria (AOB), or nitrifiers.

2.2.2.2.1. Kinetic

Operation and design conditions impact nitrification kinetics. These conditions include the physicochemical characteristics of water, characteristics of the filter media, the composition and population of nitrifying bacteria inhibitors, and the effect of backwashing (Afcharian et al., 1997). Based on previous studies (Watson and Hornburg, 1989), temperatures in the range 25–30°C at pH 7.5–8.0 favor bacterial growth for the conversion of ammonia to nitrites (Equation 2.2) and that of nitrites to nitrates (Equation 2.3):

$$NH_3 + 3/2\ O_2 \rightarrow NO_2^- + H^+ + H_2O \qquad \text{(Equation 2.2)}$$

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^- \qquad \text{(Equation 2.3)}$$

These equations show the significant role of dissolved oxygen. Oxygen, as the electron acceptor in the nitrification process, is a prerequisite for this process; the oxidation of 1 mg/L of NH_4^+ requires the consumption of 3.6 mg/L of oxygen (Lájer, 2012; Metcalf & Eddy Inc. et al., 2014). Other studies have emphasized the importance of temperature in ammonia removal, because the amount of ammonia in source water is increased at low temperatures and, with the slow activity of bacteria at such temperatures, nitrification is drastically reduced (Andersson et al., 2001; Kors et al., 1998). The acidity (pH) can also impact nitrification by changing the balance of ammonia and ammonium, as well as causing inorganic carbon losses by CO_2 deficiencies at low pH. The optimal growth and activity of nitrifiers are observed at pH 7–8 (Sharma and Ahlert, 1977).

The nitrifying bacteria species also affect the production of nitrites and nitrates. Watson, and Hornburg (1989) showed that the production of the majority of nitrites and nitrates depends on the presence of autotrophic nitrifying bacteria; however, identifying the bacteria involved in nitrification is a complicated process (Hovanec and DeLong, 1996). The attachment of bacteria to the filtration medium requires sufficient attachment sites. Macroporous BAC provided more attachment sites than microporous BAC in the second BAC filtration stage and lower temperatures, yielding higher ammonia removal (Merlet et al., 1992) and in the first filtration stage at 20°C (Afcharian et al., 1997). The attachment and detachment of biomass during filtration and backwashing are significant in nitrification. Backwashing may benefit nitrification in sand filtration by reducing biomass decay by controlling grazing, but it may also cause detachment and loss of nitrifiers (Çeçen and Aktas, 2012). Backwashing first-stage filters with open-superstructure

GAC increases ammonia removal in warm water (>18°C) but decreases nitrification in cold water (<4°C) under identical conditions. In the backwashing of first-stage filters containing closed-superstructure GAC, the ammonia removal capacity is decreased after backwashing in warm water (>18°C). Backwashing filters in the full-scale second stage showed reduced nitrification for both open- and closed-superstructure GAC at temperatures of 8–12°C (Laurent et al., 2003).

2.3. Ion Exchange

In IEX, an ion is exchanged between resin beads (the medium) and the contaminants in the solution. As mentioned in section 1.1.1, different IEX methods have been studied for removing NOM from drinking water. Each method shows disadvantages and deficiencies regarding its capability for removing different NOM fractions. For LMW compounds in general, adsorption methods (PH-S and Symons, 1991) are more effective than coagulation (Edzwald, 1993).

2.3.1. Different types of ion exchange

Synthetic IEX resins are classified into four groups, based on the functional groups bonded to the polymer backbone. The term "strong" refers to the electrolyte strength in which the functional group retains its ionic form regardless of the pH range:

1. Strong-acid cation (SAC) resins: the charged sulfonate group ($[RSO_3^-]$) is the functional group. The functional group for these resins with $pK_a < 0$ is anionic at all pH (1–14) and easily gives up protons. The applicable regenerating ions for this category of resins are H^+ and Na^+.
2. Weak-acid cation (WAC) resins: the charged carboxylate group ($[RCOO^-]$) is the functional group. The functional group with pK_a 4–5 only donates protons at pH >6. For pH 10–11, WAC has the highest apparent capacity, equal to the total capacity. The regenerating ion applied for these resins is usually H^+.
3. Strong-base anion (SBA) resins: charged quaternary amine groups of two types. The functional group of SBA type I is $[R(CH_3)_3N^+]$, while that for SBA type II is $[R(CH_3)_2(CH_3CH_2OH)N^+]$. The functional groups of this resin category, with $pK_b > 13$, are positive at pH <13 and capable of donating hydroxide ions. The applicable regenerating ions for this category are usually OH^- and Cl^-. The main structural difference of these two types of resins is the presence of ethanol in the functional group of type II. In addition, the

chemical stability of type I is slightly higher than that of type II, while the regeneration efficiency and capacity of type II are slightly higher than those of type I.

4. Weak-base anion (WBA) resins: tertiary amine groups ($[R(CH_3)_2N]$) without permanent fixed positive charges. The functional group with pK_b of 5.7–7.3 only donates hydroxide ions at pH 6.7–8.3 at 25°C. The applicable regenerating ion for this category is usually OH^- (Crittenden et al., 2012; Montgomery, 1985).

Considering the negative charge of NOM, IEX between resin beads and natural organic compounds is typically anionic. Several anion exchanges with different characteristics of structure, size, and water content have been studied to obtain a better understanding of their capability to remove different fractions of NOM. Afcharian et al. (1997) studied the impacts of two anion exchanges with strong bases for water from the Seine River. The source water was nitrified by continuous filtration. The source water contained 1.9–2.7 mg/L DOC and 0.5–0.8 mg/L BDOC with pH 7.3–8.6 at the temperature of 20°C. The results indicated similar performance by both resins in UV_{254} removal (Table 2.4).

Table 2.4: Anion exchange resins studied at Afcharian et al. (1997) project

Resin	Type	Pores	Structure	Exchange capacity (Eq/L)	Water content (%)	UV_{254} removal% Seine River
Lewatit S6328A	Strong base	Macroporous	Styrene	0.8	58-63	93
Lewatit MP 500	Strong base	Macroporous	Styrene	1.1	61-63	90

Croué et al. (1999) investigated the performance of three anion exchange resins on the removal of NOM fractions. The intake of this project was from the Suwannee River; the experiments were conducted at pH 7.4. They concluded that, in terms of NOM removal, strong anion exchange is more efficient than weak anion exchange. In addition, they proved that the molecular weight of NOM is reciprocally related to the affinity with the anion exchange resin. The removal of the hydrophobic fraction of NOM was demonstrated to be directly influenced by ionic strength, while the increase of pH had an adverse effect on the removal of the hydrophilic fraction of NOM (Table 2.5).

Another study evaluated studied a large number of resins fed by two water sources (Bolto et al.,

2004; Bolto et al., 2002). The results indicated that anion exchange resins with higher water contents and open structures showed the highest removal efficiency for any type of NOM, whether hydrophobic or hydrophilic, especially for the small molecular fraction of aquatic NOM. Resins with quaternary ammonium functional groups also offered better results in NOM removal (Table 2.6).

Another study investigated the behavior of NOM removal for different applied concentrations of three types of anion exchange resins. Specific ultra-violet absorbance (SUVA) removal was evaluated at different resin dosages (0–600 mg/L) for two water sources (Tan and Kilduff, 2007; Tan et al., 2005). The resins were backwashed with deionized water to prepare uniform low-density resin beads. The resin performance was evaluated for the two sources of the Tom Hannock Reservoir in Troy, NY, with 3.3 mg/L DOC, 0.069 cm^{-1} UV_{254}, and SUVA 2.1 L/mg DOC at pH 7 and Myrtle Beach, FL, with 20.2 mg/L DOC, 0.939 cm^{-1} of UVA_{254}, and 4.7 L/mg SUVA at pH 7.2 (Table 2.7). Strong base resins (Dowex 11 and Dowex MSA 1) performed highly and equally compared to a weak base resin (Imac HP 661).

Another study evaluated the performance of four strong anion exchange resins fed by a high-DOC river (5.6–6.7 mg/L DOC, from the Villejean/Rennes drinking water treatment plant) (Humbert et al., 2008; Humbert et al., 2005; Humbert et al., 2005b). They reported similarly effective performances from all tested resins after 30 and 45 min, in which magnetic IEX (MIEX) showed good removal of the HMW fraction of NOM and UV-absorbing organics refractory to coagulation (Table 2.8).

Cornelissen et al. (2008) studied the performance of resins which were named A through I to maintain confidentiality. The feed water contained 5.9 mg/L TOC and was sourced from the surface water treatment plant at Weesperkarspel (Netherlands). In the first coagulation step, $FeCl_3$ was added to the water; the water was then passed through rapid sand filtration. The water was removed from the lake every two weeks and stored at 5°C to prevent bacterial growth. Cornelissen et al. (2008) confirmed Bolto's findings on the importance of water content. They also proved that with smaller resin size, higher NOM removal is obtained. The removal of humic substances and building blocks, caused by ionic interaction, was increased with excess resin concentration, while the removal of neutral organic substances, caused by physical adsorption, showed no changes with excess resin concentration. The removal of NOM fractions for these resins is summarized in Table

2.9.

Graf et al. (2014) studied the efficiency of seven anion exchange resins mixed at 50, 100, 150, and 200 rpm for 30 min and allowed to settle for 5 min. They collected the samples after 5, 10, 15, and 20 min of mixing time without settling and after 30 min with 5 min settling. The best results for 2 ml/L of resins, equal to 500 bed volumes (BV), were achieved with the mixing rate of 200 rpm. The resin performance results are summarized in Table 2.10.

Table 2.5: Anion exchange resins studied by Croué et al. (1999)

Resin	Type	Functional group	Pores	Structure	Exchange capacity (Eq/L)	Water content(%)	Removal%*				
							HPA	TPA	Char	Neut	uHA
Dowex 11	Strong base	Quaternary amine	Gel	Styrene-DVB	1.2	52-60	40	68	70	78	8
Dowex MSA 1	Strong base	Quaternary amine	Macroporous	Styrene-DVB	1.0	56-64	38	66	70	78	12
Imac HP 661	Weak base	$-N(R)_2$	Macroporous	Styrene-DVB	1.4	50-58	32	40	42	45	6

*HPA: hydrophobic acids

TPA: transphilic acids

Char: charged hydrophilic compounds

Neut: neutral hydrophilic compounds

uHA: Ultrahydrophilic acids: colloidal in nature

Table 2.6: Anion exchange resins studied by Bolto et al. (2002) and Bolto et al. (2004)

Resin	Type	Pores	Structure	Exchange capacity (Eq/L)	Water content (%)	UV_{254} removal %	
						Horsham*	Aldrich*
Amberlite IRA 420	Strong base	Gel	Styrene	1.2	43	N/A	19
Amberlite IRA 410	Strong base	Gel	Styrene, type II	1.3	43	77	32
Lewatit MP 500	Strong base	Macroporous	Styrene	1.6	43	N/A	20
Amberlite IRA 400	Strong base	Gel	Styrene	1.4	45	57	14
Amberlite CG 400	Strong base	Gel	Styrene	1.4	45	N/A	22
Imac HP 555	Strong base	Macroporous	Styrene, -NEt3+	0.9	49	58	20
Amberlite IRA 402	Strong base	Gel	Styrene	1.3	54	N/A	26
Purolite A520E	Strong base	Macroporous	Styrene, -NEt3+	1	54	N/A	30
Amberlite IRA 910	Strong base	Macroporous	Styrene, type II	1.1	55	73	33
Amberlite IRA 401	Strong base	Gel	Styrene	0.8	56	N/A	24

Table 2.6: Anion exchange resins studied by Bolto et al. (2002) and Bolto et al. (2004) (continued)

Resin	Type	Pores	Structure	Exchange capacity (Eq/L)	Water content (%)	UV_{254} removal %	
						Horsham*	Aldrich*
Amberlite IRA 904	Strong base	Macroporous	Styrene	0.7	57	N/A	43
Amberlite IRA 458	Strong base	Gel	Acrylic	1.2	60	69	47
Amberlite IRA 900	Strong base	Macroporous	Styrene	1	60	N/A	42
Amberlite A 26	Strong base	Macroporous	Styrene	1	61	N/A	63
Amberlite IRA 958	Strong base	Macroporous	Acrylic	0.8	69	73	92
Amberlite IRA 938	Strong base	Macroporous	Styrene	0.5	73	N/A	78
ResinTech SIR 22P	Strong base	Gel	Styrene	0.4	75	84	59
CSIRO MASB	Strong base	Macroporous	Methacrylic	0.4	80	89	N/A
CSIRO PDAA	Strong base	Gel	Diallylamine	0.3	90	91	N/A
Reillex 425	Weak base	Macroporous	Pyridine	0.7	50	53	N/A
Amberlite IRA 938	Weak base	Macroporous	Styrene	0.9	58	55	N/A
Amberlite IRA 68	Weak base	Gel	Acrylic	1.2	59	58	N/A
Amberlite IRA 35	Weak base	Macroporous	Acrylic	1.1	69	61	N/A
CSIRO MAWB	Weak base	Macroporous	Methacrylic	0.7	37	55	N/A

*Water Sources

Table 2.7: Anion exchange resins studied by Tan et al. (2005) and Tan, and Kilduff (2007)

Resin	Type	Functional group	Matrix	Structure	Exchange capacity	Water content (%)	SUVA removal%*	
							TKM	MB
Marathon A	Strong base, Type I	Trimethylamine	Gel-typr	Styrene-DVB	1.3	50-60	30	failed
Dowex M-43	Weak base	Polyamine	Macroporous	Styrene-DVB	1.55	40-50	18	failed
Marathon 11	Strong base, Type I	Quanternary amine	Gel	Styrene-DVB	1.3	48-58	20	failed

*TKM: Tom Hannock Resorvoir, Troy, NY

MB: Myrtle Beach, Sc

Table 2.8: Anion exchange resins studied by Humbert et al. (2005), Humbert et al. (2008) and Humbert et al. (2005b)

Resin	Type	Matrix	Structure	Exchange capacity	Water content(%)	Particle size (mm)	Removal%		
							DOC	SUVA	UV
MIEX	Strong base	Macroporous	Acrylic	N/A	N/A	0.15-0.18	79	67	93
DOWEX-11	Strong base	Gel	Styrene	1.3	48-58	0.55 ±0.5	91	64	97
DOWEX-MSA	Strong base	Macroporous	Styrene	1.1	56-66	0.64 ±0.6	85	61	94
Amberlite IRA 958	N/A	N/A	N/A	N/A	N/A	0.63	82	59	N/A
AmberSORB	N/A	N/A	N/A	N/A	N/A	Carbonaceous resin	76	18	N/A

Table 2.9: Anion exchange resins studied by Cornelissen et al. (2008)

Resin	Type	Pores	Structure	Exchange capacity (Eq/L)	Water content (%)	Particle size	Removal%*			
							TOC	Humics	BB	Neutrals
A	Weak base	Macroporous	Styrene	1.55	45	0.75	10	3	17	46
B	Strong base - type I	Macroporous	Styrene	1.1	62	0.65	44	47	33	62
C	Strong base - type I	Gel	Acrylic	1.25	58	0.53	44	53	25	54
D	Strong base - type I	Gel	Styrene	-	78	0.5	39	50	17	54
E	Strong base - type I	Macroporous	Styrene	1	61	0.7	29	34	17	54
F	Weak base	Macroporous	Acrylic	0.8	69	0.74	36	47	8	54
G	Strong base - type I	Gel	Styrene	1.3	55	0.58	17	13	33	46
H	Strong base - type I	Macroporous	Styrene	0.8	67	0.81	32	38	33	54
I	Strong base - type I	Macroporous	Acrylic	0.8	69	0.68	36	44	25	54

*BB= Building Blocks

Table 2.10: Anion exchange resins studied by Graf et al. (2014)

Resin	Type	Functional group	Pores	Structure	Exchange capacity	Water content(%)	Particle size(mm)	C/ C_0	
								UV_{254}	DOC
MIEX	Strong base	Quaternary amine	Macroporous	Acrylic	~ 0.5	NP	0.2	0.3	0.5
Dowex Marathon 11	Strong base, type I	Quaternary amine	Gel	Styrene	1.3	48-58	0.55	0.71	0.75
Dowex Tan-1	Strong base, type I	Quaternary amine	Macroporous	Styrene	0.7	70-82	0.81	0.71	0.72
Purofine PFA444	Strong base, type I	Quaternary amine	Gel	Styrene	1.1	50-60	0.57	0.69	0.72
Purolite A500P	Strong base, type I	Quaternary amine	Macroporous	Styrene	0.8	63-70	0.75	0.9	0.9
Tanex	Strong base	Quaternary amine	Macroporous/Gel	Styrene	NP	68-75	0.75	0.73	0.77
Purolite A850	Strong base	Quaternary amine	Gel	Acrylic	1.25	57-62	0.75	0.72	0.75

The latest study on resin performance for NOM removal was conducted by Bazri (2016), who compared six anion exchange resins (strong bases and weak bases) at the dosage of 100 mg/L for 8 h of contact time. The resins were fed with Mille Iles River (Qc, Can), which had the high TOC of 6.0 mg/L, SUVA of 4.39 mg/L, and moderate turbidity of 5.0 NTU (Bazri et al., 2016). In addition to the efficacy of these resins in TOC removal, their mechanical properties such as settling velocity and their availabilities from their manufacturers were used to rate the resins. Considering the fastest settling velocity of Purolite A860 and its high TOC removal capacity, Purolite A860 was reported as the resin with the best performance in NOM removal from surface water (Bazri et al., 2016) (Table 2.11).

Table 2.11: Anion exchange resins studied by Bazri et al. (2016)

Resin	Type	Functional group	Pores	Structure	Exchange capacity	TOC/TOC_0
Amberlite IRA 458	Strong base	Quaternary amine	Gel	Polyacrylic	>1.25	0.24
Purolite A860	**Strong base**	**Quaternary amine**	**Macroporous**	**Polyacrylic**	**0.8**	**0.18**
Ionac Maro-T	Strong base	Quaternary amine	Macroporous	Polyacrylic	1.1	0.18
Lewatit VPOC 1071	Strong base	Quaternary amine	Gel	Polyacrylic	1.25	0.31
Purolite A847	Weak base	Tertiary amine	Gel	Polyacrylic	>1.6	0.20
Lewatit VPOC 1073	Weak base	Tertiary amine	Gel	Polyacrylic	>1.25	0.25

2.3.2. Kinetic

IEX is a sorption process. To model the kinetics, two approaches are available: either a mechanistic approach describing the entire system using equations and solving these equations using MATLAB software, or an empirical approach describing exchange activity. Sorption occurs in the mass transfer zone (MTZ) in which the reactions take place (Figure 2.4); this is where the kinetics are studied. In a column, the MTZ gradually moves to the bottom. This means that the entire top level is completely exhausted; no fresh layer or MTZ remains to remove contaminants. Therefore,

concentration begins in the effluent when the MTZ reaches the bottom of the column.

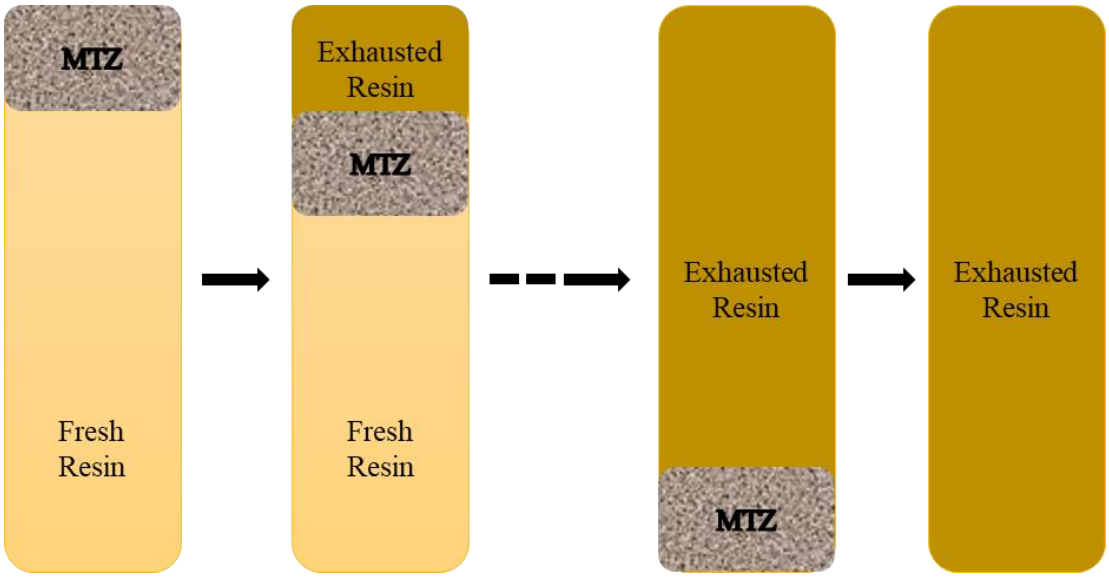

Figure 2.4: Mass transfer zone in time

In a deep column, the exhaustion of all media takes time, depending on the contaminants and their affinity with the media. For some contaminants of smaller size, the column height is short and exhaustion occurs very quickly, but for other contaminants like NOM with large molecules, exhaustion takes longer time and the column requires a height of 2–3 ft.

The equation below (Equation 2.4) presents the basic equation to model the kinetics of advection–diffusion–sorption (Kantzas et al., 2015):

$$K_L \frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} + \frac{(1-\phi)\rho_r}{\phi}\frac{\partial q}{\partial t} \qquad \text{(Equation 2.4)}$$

in which,

q = amount adsorbed (mass of solute per unit mass of solid),

φ = porosity,

ρ_r = solid (grain) density (mass of solid per unit volume).

For fast adsorption, comparable to convective mass transfer, $\frac{\partial q}{\partial t}$ is considered as $\frac{\partial q}{\partial c}\frac{\partial c}{\partial t}$, allowing the

modification of Equation 2.4 to:

$$K_L \frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} = \left[1 + \frac{(1-\phi)\rho_r}{\phi}\frac{\partial q}{\partial c}\right]\frac{\partial c}{\partial t} \quad \text{(Equation 2.5)}$$

For NOM removal, a study on different resin dosages and various contact times showed that, based on the pseudo-first-order kinetic model ($q_t = q_e(1 - e^{-k_1 t})$ (Boyd et al., 1947), pore diffusion model, and film diffusion models, the best DOC removal (reaching 80%) occurs for 10–15 mL resin/L and 30–45 min of contact time. The results showed that high resin dosages and extended contact times could not remove the remaining DOC (19–43%, corresponding to 0.7–2.8 mg/L). Using the Biot number, pore diffusion was identified as the limiting factor for DOC removal (Bazri and Mohseni, 2016) .

Kinetic experiments on a strongly basic resin (Purolite A860) and a weakly basic resin (Purolite A847) regarding the impact of resin properties on NOM removal kinetics showed no important differences in their performances. A slightly higher capacity and affinity for organic molecules was observed in Purolite A860 in an isotherm test (10%) and higher TOC removal by Purolite A860 was observed under multiple consecutive loadings, as compared to Purolite A847 (Bazri et al., 2016). NOM properties affect the kinetics of removal; TOC is better removed as smaller-molecular-weight organics rather than as larger HA molecules (Bazri and Mohseni, 2016).

2.3.3. Regeneration

As NOM is removed from the water, the resin pores are occupied by NOM until resin exhaustion occurs. To regain IEX capacity, frequent regeneration (every 24–72 h) is normally performed. Two methods of column regeneration are suggested: co-flow regeneration (CFR) and reverse-flow regeneration (RFR). The CFR function is based on top-to-bottom flow during operation and regeneration. This method requires a larger volume of reagents to regain the resin capacity at the bottom of the column. The RFR function is based on regeneration by flow in the direction opposing normal flow operation. Thus, the less exhausted layer is regenerated first and becomes the cleanest layer for the next operation. In addition, because contaminants do not flow throughout the column during regeneration, RFR requires lower reagent amounts than CFR method.

One common and efficient method to regain the capacity of exhausted strong base resins uses brine (NaCl 10% W/V) as the regenerant, which is costly (NSF-certified salt costs approximately

$0.30/kg in the region of Montreal). Infrastructure is required to manage brine production of 20–36 kg NaCl per 1000 m^3 of treated water (Grefte et al., 2013) or 160 kg NaCl per 1 m^3 resin[1]. This large volume of brine ends in environmentally unfriendly disposal (Clifford, 1999; Rokicki and Boyer, 2011). It has also been recommended[2] to combine NaOH 2% with NaCl 10%, realizing extra cleaning efficacy; this technique is often referred to as a brine squeeze. Another efficient regenerant for this purpose is bicarbonate salt ($NaHCO_3$), the disposal of which is environmentally friendly, but its higher price ($3.13/1,000 gal of water treated) is disadvantageous (Ishii and Boyer, 2011; Ness and Boyer, 2017; Rokicki and Boyer, 2011; Walker and Boyer, 2011). The advantages and disadvantages of NaCl and $NaHCO_3$ are summarized in Table 2.12.

Table 2.12: Regenerant's comparison

Regenerant	Pros	Cons	Cost ($/1000 gal)
Brine (NaCl 10% wt)	Efficient	Large volume of disposal (20-36 kg NaCl/ 1000 m^3 treated water)	$1.07/1,000
$NaHCO_3$ (Bicarbonate salt)	Environmentally benign/ No excess chloride in treated water	Expensive	$3.13

2.3.4. Limitations of ion exchange

Although IEX offers high NOM removal, the removal of contaminants is dependent on the resin type. Regarding the charge of the contaminants, anionic exchange resins cannot remove positively charged micropollutants. For the current study, using negatively charged IEX resin (Purolite A860), ammonia and other positively charged contaminants cannot be removed simultaneously. The rapidly exhausted resin beads require frequent regeneration, which produces significant volumes of brine requiring disposal in the environment. Overall, process improvements are necessary in order to minimize the need for regeneration.

2.3.5. Biological ion exchange

Considering the pros and cons of BAC and IEX, an alternative method for NOM and ammonia removal of BIEX was proposed. Winter et al. (2016) investigated the performance of BIEX at the

[1] www.purolite.com/product/a860
[2] https://www.purolite.com/dam

laboratory scale with raw water from Jericho Pond (1-µm pre-filtered water, diluted with tap water to a constant DOC concentration of 5 mg C/L). The setup consisted of three abiotic and three biotic columns of 0.1 m in height filled with Purolite A860 resin. The abiotic columns were tested by injecting sodium azide into the feed water. Monthly backwash and regeneration processes were run by three different methods of regeneration with brine (100 g NaCl/L) and regeneration with caustic and brine (20 g NaOH/L and 100 g NaCl/ L), with and without resin pre-disinfection with peracetic acid. After regeneration, the resin beads lost 5–10% of their capacity. However, based on the results, the type of regeneration did not affect the recovered capacities of the resin beads. After two months of operation, the results indicated an average of 60–62% DOC removal by the biotic columns, while the abiotic columns removed 39–42% DOC. The NOM fractions removed by the biotic and biotic columns are summarized in Table 2.13.

Table 2.13: Removed NOM fraction based on Winter et al. (2016) study

NOM fraction	Abiotic	Biotic	Comments
Larger humic substance	✓	✓	Main foulants in low-pressure membrane filter
Small humic substance	X	✓	-
Building blocks	X	✓	Biodegradable
Low-molecular weight acids	X	partially	Biodegradable
Biopolymer	<15%	<15%	Mostly macromolecular NOM

CHAPTER 3 METHODOLOGY AND EXPERIMENTAL PLAN

3.1. Experimental approach

The objective of the current research is to study BIEX performance in comparison to IEX and BAC in removing NOM and ammonia from natural surface waters. To accomplish this, four columns were operated in parallel with different media: GAC, BAC, BIEX, and IEX.

Table 3.1 summarizes the differences in the conditions of this project compared to previous studies on BIEX filtration.

Table 3.1: Conditions of current study differing from conditions used by Schulz et al. (2017) and Winter et al. (2018) for the study of BIEX

Schulz et al. (2017)	**Winter et al. (2018)**	**Current Study**
Lab- scale experiment	Lab- scale experiment	Pilot- scale experiment
3 Abiotic columns 3 Biotic columns	2 BIEX columns 2 BAC columns	1 IEX column 1 BIEX column 1 GAC column 1 BAC column
Modeled raw water (1 µm filtered - Constant DOC : 5 mg/L)	Modeled raw water (1 µm filtered - Constant DOC : 5 mg/L)	Colored and turbid natural surface water, unfiltered
Room temperature	Room temperature	Temperature depends on seasonal changes
Monthly regeneration (Abiotic and Biotic)	No regeneration	Weekly regeneration for IEX column; Regeneration after 331 days for BIEX
NOM removal	NOM removal	NOM removal Ammonia removal
Operated for 2 months 2800 BV	Operated for ≈11 months 16 000 BV	Operated for 442 days 21 216 BV
Sampling of Effluent	Sampling of Effluent	Weekly sampling of effluent; Sampling in particular different depths of filters to study kinetic

3.1.1. Location and water matrix

The column setup was located at the Pont-Viau drinking water treatment plant (DWTP) in Laval, QC, Canada (Figure 3.1). The columns were directly fed with raw water from the des Prairies River.

Figure 3.1: Location of the experimental plan

The experiment was started in cold temperature conditions (February 28th, 2017) and continued until May 15th, 2018. The BIEX was operated without regeneration until January 23, 2018. It was then regenerated and operated until the end of the study. The characteristics of the source waters are summarized in Table 3.2 .

Table 3.2: Source water characteristics (February 28th, 2017 – May 15th, 2018)

Parameters	Temperature (˚C)	Turbidity (NTU)	DOC (mg/L)	TOC (mg/L)	UVA	pH
Number of samples	54	53	51	25	49	54
Max	23.6	58	7.89	8.36	0.275	8.66
Min	1.4	3.13	5.81	6.81	0.193	6.69
Average	10.2	14.27	6.97	7.45	0.243	7.39

3.1.2. Pilot plant description

Figure 3.2 presents a schematic of the experimental setup, comprising four down-flow polyvinyl chloride (PVC) pilot-scale columns of 2 m in height and 10 cm in diameter. All columns were filled to 100 cm depth with the various media. The effluent was recovered through a nozzle that was also used for air or water injection during the weekly backwash process.

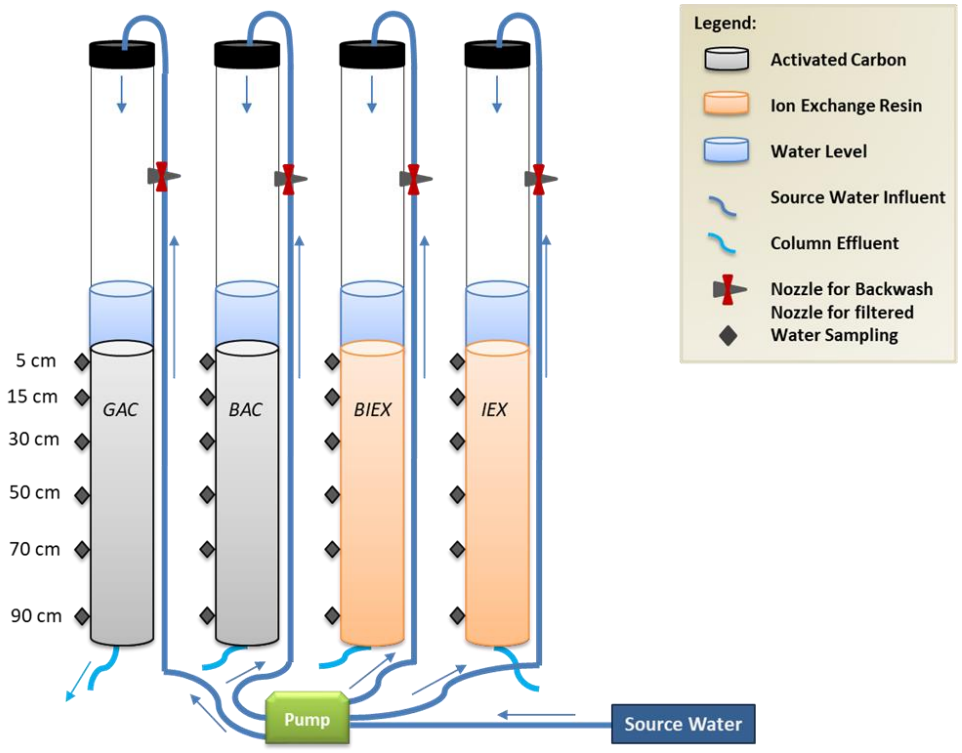

Figure 3.2: Schematic of the experimental set-up

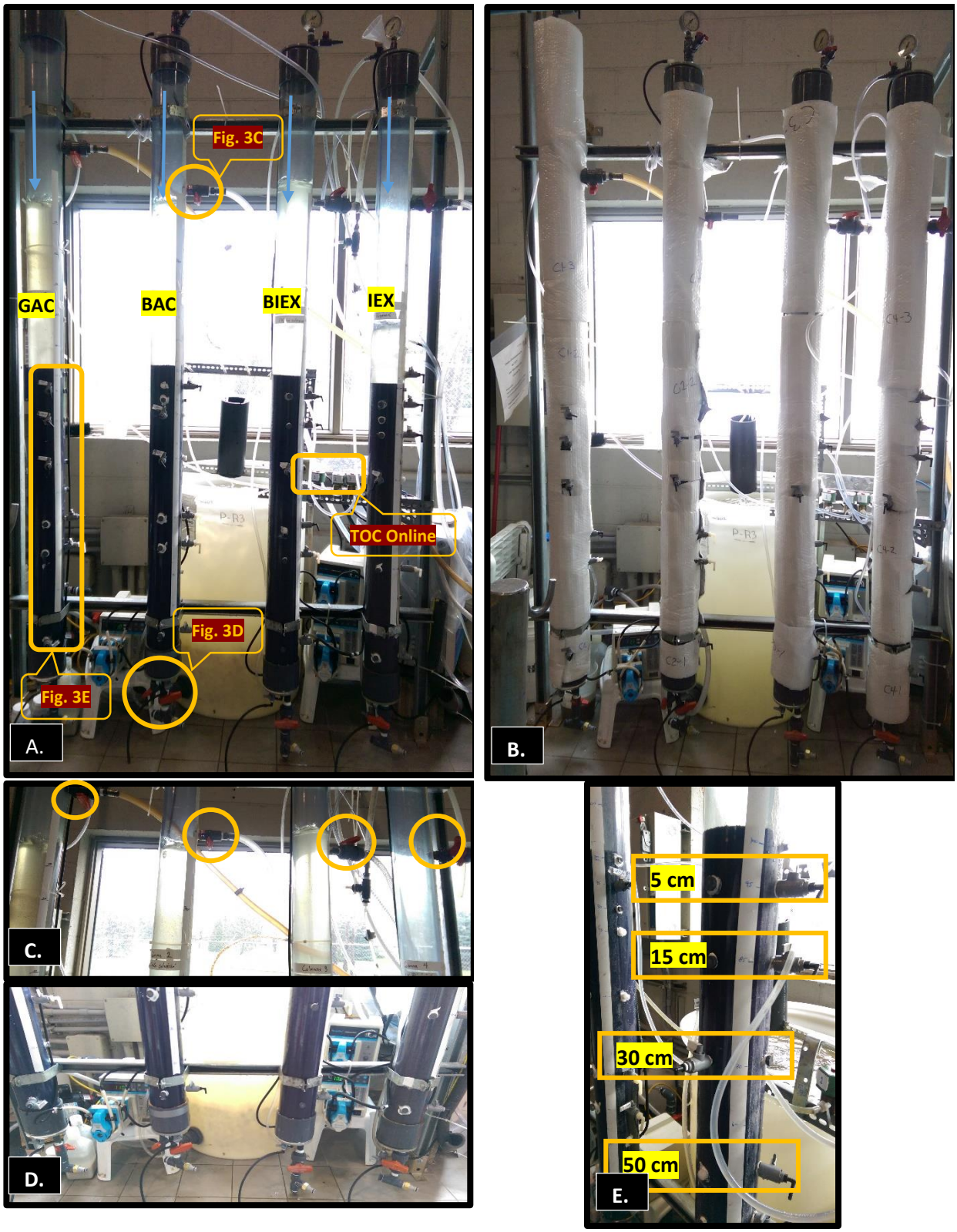

Figure 3.3: (A) Experimental Set-up, (B) Isolated set-up from heat, cold and light, (C) Backwash outlet valves, (D) Effluent and backwash inlet valves, (E) Liquid and solid sampling points.

All columns (Figure 3.3) were operated at the same down-flow velocity of 2 m/h (2 BV/h), equal to a flowrate of 270 mL/min and the EBCT of 30 min. In order to investigate the mechanism kinetics, each column was equipped with liquid and solid sampling taps at depths of 5, 15, 30, 50, 60, and 90 cm, corresponding to the EBCTs presented in Table 3.3. The TOC concentrations of filtered water samples from each column were monitored using an online TOC-meter (Sievers 900 On-Line TOC Analyser, GE Water).

Table 3.3: Sampling points

Depth (cm)	5	15	30	50	60	90	100
EBCT (min)	0.15	4.5	9	15	18	27	30

The 100 cm of media corresponds to 8.10 liters of media. Two columns were filled with AC (Weststate Aquacarb 816) in different conditions (new GAC or BAC). The BAC media was recovered from one of the filters from the plant. It had been fed with settled and ozonated waters for a period of >1 year. The other two columns (IEX and BIEX) were filled with fresh strong-base IEX Purolite A860 resin. The IEX column was regenerated weekly according to the conditions described in Table 3.4, while the BIEX column was operated without regeneration.

Backwashing of columns was performed weekly after sampling. First, air was injected for 2 min to break the accumulated biofilm. Then, water was injected for 10–30 min depending on the material density (the IEX and BIEX columns required longer backwash times at lower velocities to control the resin expansion). In order to preserve the parallel nature of operation for all columns, the media expansion of 50% was chosen. To maintain approximately 50% media expansion, the water injection rate was controlled by visual metering by regulating the injection nozzle, regardless of any seasonal factors. For the backwashing of each column, 40 L of filtered water was consumed. In addition, to regain the resin capacity for the IEX column, weekly regeneration was operated using 100 g/L NaCl as regenerant. **The BIEX filter was regenerated only once after 331 days of operation** following the same method of regeneration used for the IEX filter. More details regarding the backwashing and regenerant conditions are provided in Table 3.4 and Table 3.5, respectively.

Table 3.4: Pilot design and operation

Parameters			Column 1	Column 2	Column 3	Column 4
Description			New BAC	Aged BAC	BIEX	IEX
Media	Type		Activated carbon	Activated carbon	Resin	Resin
	Product name		Weststate Aquacarb 816	Weststate Aquacarb 816	Purolite A860	Purolite A860
	Supplier		Evoqua	Evoqua	Purolite Company	Purolite Company
	Effective size		1.4 mm	1.4 mm	557 micron	557 micron
	Age		New	1 year old	New	New
	Details on ageing conditions		-	1 year fed by settled-ozonated waters	-	-
	Other		8.1 L of media	8.1 L of media	8.1 L of media	8.1 L of media
Column diameter			4"	4"	4"	4"
Filter bed depth (m)			1 m	1 m	1 m	1 m
Empty bed contact time (min)			30 min	30 min	30 min	30 min
Filtration rate			1.6-2 m/h	1.6-2 m/h	1.6-2 m/h	1.6-2 m/h
Backwash	Rate (duration)	Air	2 min	2 min	2 min	2 min
		Water (after air injection)	8-10 min	8-10 min	8-10 min	8-10 min
	Frequency		Weekly	Weekly	Weekly	Weekly
	Expansion		50%	50%	50%	50%
	Other details on equipment used (nozzle)		Nozzle	Nozzle	Nozzle	Nozzle

Table 3.5: Regeneration conditions for ion exchange

	Parameters	Column 3	Column 4
	Description	**BIEX**	**IEX**
IEX regeneration (down-flow)	**Brine concentration**	100 g/L NaCl	100 g/L NaCl
	Brine volume	20L	20L
	Water used to prepare brine	Service water	Service water
	Brine dilution	filtered water	filtered water
	Flow rate	2BV/h	2BV/h
	Duration	≈60 min	≈60 min
	Rinsing	with filtered water until conductivity reaches 2000 uS/cm; fast rinse total max of 9BV, 2BV/h for 30 min than 5BV/h for 30 min	
	Frequency	After one year (considering the BIEX Performance)	weekly (if effluent TOC≤ 2 mg/L)
	Brine disposal	-	Drain/Reuse

3.1.3. Analytical methods

In order to study the performance of the columns investigated in this project, various parameters were monitored and evaluated by weekly sampling and seasonal profile sampling. On the next page, Table 3.6 presents an overview of the sampling schedule with the list of investigated parameters. The following paragraphs detail the investigation methods.

Factors involved in filter performance:

3.1.3.1. Temperature, turbidity and pH

Temperature, turbidity and pH were measured using field equipment (Temperature: VWR digi-thermo, Turbidity: HACH 2100Q, pH: HACH HQ40d).

3.1.3.2. Ion exchange analysis

Monitoring the capacity of IEX for the IEX and BIEX filters allowed understanding of the performance mode of the BIEX column. In addition, it helped to prove the possibility of organic composition removal by BIEX after IEX exhaustion. The IEX capacity was determined by the *Practical Resin Capacity Method* (Veolia, 2014). The released chloride contents from the IEX and BIEX filters by the exchange of ions were also monitored by ionic chromatography (ICS 5000 AS-DP DIONEX Thermo Scientific) to prove the function and exhaustion of IEX.

3.1.3.2.1. Ion exchange capacity:

The anion exchange capacities (AECs) of IEX and BIEX resins were monitored by titration. IEX beads (10 mL) were added into 170 mL $NaNO_3$ (25.6 g/L), which was agitated at 190 rpm for 30 min to displace Cl^- by NO_3^-. The beads were then removed. An aliquot of the filtrate (15-30 mL) was spiked with 1 mL of K_2CrO_4 (20 g/L) and then titrated with $AgNO_3$ (0.04 N) until the solution became orange in color because of AgCl precipitation. The AEC is expressed as mEq/mL of resin.

$$[Cl^-] = \frac{V_{AgNO_3} \times M_{AgNO_3}}{V_{titration\ sample}} \times \text{molar mass}_{Cl^-} \qquad \text{(Equation 3.1)}$$

$$Cl^-(eq) = \frac{[Cl^-]}{\text{molar mass}_{Cl^-}} \times \frac{V_{NaNO_3}}{1000} \qquad \text{(Equation 3.2)}$$

$$\frac{V_{exchanged\ Cl^-}}{V_{resin}} = \frac{Cl^-(eq) \times \text{molar mass}_{Cl^-}}{V_{resin}} \times 1000 \qquad \text{(Equation 3.3)}$$

$$\text{IEX Capacity } \left(\frac{\text{meq resin}}{\text{ml resin}}\right) = \frac{V_{\text{exchanged } Cl^-}}{V_{\text{resin}} \times \text{molar mass}_{Cl^-}} \quad \text{(Equation 3.4)}$$

Considering the volumes of the titration sample (20 mL), resin sample (25 mL), and $NaNO_3$ (500 mL) in multiplying the equations above, the summarized equation for AEC is as follows (Equation 3.5).

$$\text{IEX Capacity } \left(\frac{\text{meq resin}}{\text{ml resin}}\right) = V_{AgNO_3} \times M_{AgNO_3} \quad \text{(Equation 3.5)}$$

3.1.3.2.2. Chloride release:

Chloride measurement was performed by ion chromatography (IC), according to analytical method MA. 300 Ions 1.3 of CEAEQ (2014). The chloride release was calculated as follows (Equation 3.6):

$$[\text{Chloride release}] = [\text{Chloride}]_{(\text{BIEX/IEX effluent})} - [\text{Chloride}]_{(\text{Source water})} \quad \text{(Equation 3.6)}$$

The chloride release concentration is correlated with the AEC.

3.1.3.3. Biological activity analysis

various methods are available to determine and prove the growth and activity of the bacteria and the biofilm on the media. Some of these methods, such as measurements of bacteria adenosine triphosphate (ATP) and extracellular polymeric substances (EPS), monitor the entire bacteria content, some measure heterotrophic bacteria only by characterizing potential acetate uptake (PAU), potential glucose respiration (PGR), and heterotrophic plate count (HPC), and some measure autotrophic bacteria by monitoring nitrifying activity. Another method used to evaluate the amount of biodegraded carbon is the direct measurement of BDOC concentration. Among the aforementioned methods, BDOC, ATP, and nitrifying bacteria were chosen as metrics to determine the biological activity.

Table 3.6: Analytical methods

Parameter	Sample details	Equipment / Method	Sampling frequency	Sampling depth
Temperature	Raw water + column effluent	Thermometer	weekly	Effluent (100 cm)
Turbidity	Raw water + column effluent	Turbidimeter 2100N Hach	Weekly	Effluent (100 cm)
pH	Raw water + column effluent	pH meter	Weekly	Effluent (100 cm)
IEX capacity	Solid samples of IEX columns only (n=2)	Practical Resin Capacity (Veolia 2014) Strong base capacity only. Weak base is negligible.	Weekly Profile	Changing: from 15 to 50 to 90 cm depending on the resin exhaustion 15, 50, 90 cm
Chloride	Raw water + column effluent	Ion chromatography	Weekly Profile dep.	Effluent (100 cm) 15, 50, 90 cm
ATP	Solid samples of filter bed	Extraction method: inspired from Magic-Knezev, and van der Kooij (2004) study Measurements: LuminUltra ATP kit	Weekly Profile dep.	5 cm 5, 50, 90 cm
Nitrifying bacteria	Solid samples of filter bed	Section (3.1.3.3.3)	Profile dep.	5, 15, 30, 50, 60 cm
BDOC	Raw water + column effluent	Standard methods, 21st edition, 2005	Weekly Profile dep.	Effluent (100 cm) 5, 15, 30, 60, 100 cm

Table 3.6: Analytical methods (continued)

Parameter	Sample details	Equipment / Method	Sampling frequency	Sampling depth
TOC	Raw water + column effluent	Online	Continuous	Effluent (100 cm)
DOC	Raw water + column effluent	Standard Methods, 21st edition, 2005	Weekly	Effluent (100 cm)
			Profile dep.	5, 15, 30, 50, 60, 90, 100 cm
DO	Raw water + column effluent	pH meter	Weekly	Effluent (100 cm)
Colour 456	Raw water + column effluent	Filtration: same as UV measurement method Reading: 456 nm	Weekly	Effluent (100 cm)
UVA_{254}	Raw water + column effluent	UV measurement method (B. 5910 Standard Methods, 2005)	Weekly	Effluent (100 cm)
LC-OCD	Raw water + column effluent	Interest in DOC measurements - by University of Waterloo Based on method presented in (Huber et al., 2011) paper.	At time zero	Effluent (100 cm)
			At steady state (t: 51, 135 days)	Effluent (100 cm)
THM-UFC	Raw water + column effluent	GC- ECD, Method: USEPA METHOD 524.2	Weekly	Effluent (100 cm)
HAA5-UFC	Raw water + column effluent	GC-ECD, HAA Extraction Method: USEPA Method 552.2 (Incubation for 2 hours at 50°C)	Weekly	Effluent (100 cm)

Table 3.6: Analytical methods (continued)

Parameter	Sample details	Equipment / Method	Sampling frequency	Sampling depth
NH_3	Raw water + column effluent	Colorimetry with blue of indophenol	Weekly	Effluent (100 cm)
			Profile dep.	5, 15, 30, 50, 60, 100 cm
Nitrate/ Nitrite	Raw water + column effluent	Ion chromatography	Weekly	Effluent (100 cm)
			Profile dep.	15, 50, 90, 100 cm
LC-OND	Raw water + column effluent	LC_OND performed by University of Waterloo Based on method presented in (Huber et al., 2011) paper.	At time zero	Effluent (100 cm)
			At steady state (t: 51, 135 days)	Effluent (100 cm)

3.1.3.3.1. Biodegradable dissolved organic carbon (BDOC)

First, the samples were filtered by a 0.45-µm membrane into 125-mL carbon-free duplicate bottles. To avoid protozoa, the inoculum was filtered with a 2.7-µm membrane and then 2% (v/v) of filtered inoculum containing indigenous bacteria was added to the samples. Part of this sample (40 mL) was analyzed for DOC (T_0); the rest was incubated at 22°C without mixing or aeration. After 30 days of incubation, 40 mL of the remained sample was analyzed for DOC (T_{30}). The difference between T_0 and T_{30} represented the BDOC concentration.

3.1.3.3.2. Total biomass using adenosine triphosphate (ATP)

The presence and activity of the biofilm on the different media were measured by monitoring ATP. All steps were performed within a sterilized environment using sterilized equipment. The biofilm attached to the media (5 g) was first removed via sonication for 3 min in 50 mL phosphate buffer per cycle (six cycles) at a power of 20 W. The phosphate buffer was retained after each cycle, because it contained part of the detached biofilm from the extracted sample. After sonication, 30 mL of a composite was made using 5 mL of the retained phosphate buffer from after each cycle. Then, 10 mL of the composite was filtered to preserve the intracellular ATP. *UltraLyse*[*] solution was then filtered through the same filter to harvest the intracellular ATP trapped on the filter. To ensure that the syringe, filters, and phosphate buffer were sterilized, 9 mL of phosphate buffer was passed through the filter using the same method of composite filtration (named as "control negative"). To evaluate and compare the accuracy of the ATP sample values, 1 mL of only one sample composite (named "sample (1 mL)") and 1 mL of only one sample composite along with 100 µL of *UltraCheck*[*] (named "spike") were filtered separately (same filtration method). The relative luminescence units (RLU) of the solutions (Milli-Q water + UltraChec*k*) for calibration curves from concentrations of 0 to 1000 µL and of the samples were read via a TriStar^2 Multimode Reader LB 942 (BERTHOLD Technologies). *Luminase*[*] was injected automatically as an indicator. The RLU values were converted to ATP ρg/L based on the calibration curve.

The final value of the extracted sample ATP is calculated as follows (Equation 3.7):

[*] UltraLyse, UltraCheck and Luminas were provided from LuminUltra

$$\text{ATP}\left(\frac{\text{ng}}{\text{cm}^3}\right) = \frac{\text{V}_{\text{Ph.b}}(\text{ml}) \times \text{ATP}_{\text{Composite}}\left(\frac{\rho\text{g}}{\text{L}}\right)}{\text{Mass}_{\text{media}}(\text{g})} \times \rho\left(\frac{\text{g}}{\text{cm}^3}\right) \times 10^{-6} \qquad \text{(Equation 3.7)}$$

ρ: Wet density of media (for AC: 1.4 g/cm^3, for resin: 1.04 g/cm^3)

$V_{Ph.b}$: Total volume of retained phosphate buffer ≈ 300 mL

$Mass_{media}$: Mass of extracted media, taken from the pilot ≈ 5 g

3.1.3.3.3. Nitrifying bacteria

The nitrifying bacteria content was measured using the Potential Nitrification Activity method presented by Kihn et al. (2000). For the experiment, two types of solution were prepared: (i) a chelated metal solution containing 0.004 g of $CoCl_2 \cdot 6H_2O$, 0.06 g of $CuSO_4$, 1.0 g of $FeCl_3$, 0.3 g of $ZnSO_4 \cdot 7H_2O$, 0.6 g of $MnSO_4 \cdot 7H_2O$, 0.2 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and 6.0 g of ethylenediaminetetraacetic acid (EDTA) in a 1-L volumetric flask and (ii) a medium for nitrifying bacteria containing 0.05 g of $MgSO_4 \cdot 7H_2O$, 2.00 g NaCl, 0.50 g of K_2HPO_4, 0.0168 g of $NaHCO_3$, 0.037 g of NH_4Cl, and 2 mL of chelated metal solution per L. The nitrifying medium, split into 100-mL aliquots, was heated at 120°C for 30 min to reach the final volume of 5 mL. In the next step, 2 cm^3 of the media sample was washed in a 15-mL tube three times using the nitrifying solution. After adding 5 mL of the nitrifying solution, we aerated them with an aquarium pump free of trace organic matter by passing the air through a mixture of sulfo-chromic acid and Milli-Q water. We took samples in a 60-mL syringe with an autoclaved needle from un-incubated samples and samples incubated for 15 and 30 min at 30°C and then passed them through a 0.2-µm filter and stored them in 15-mL sterile vials. Then, the concentrations of nitrites and nitrates formed were measured by colorimetry.

- **Nitrites**

  Nitrite and nitrate concentrations were measured by a colorimetric method. A sulfanilamide solution was made by adding 10 g sulfanilamide, 1 g dichlorhydrated N-(1-naphthyl) ethylene diamine, and 100 mL concentrated phosphoric acid (85%) to 1000 mL Milli-Q water in a dark bottle and stored in the dark. To make a standard curve (concentration 0.000 to 0.210 mg $N\text{-}NO_2$/L), the mother-solution (stock standard) of nitrite 140 mg $N\text{-}NO_2$/L and daughter-solution (working standard) were made of 0.690 g $NaNO_2$ in 1000 mL Milli-Q water and 10 mL of the mother-solution in 100 mL Milli-Q water,

respectively. Measurements were performed under 540-nm radiation in a 1-cm spectrophotometric cell with 2 mL of the sample or standard and 0.150 mL of the sulfanilamide solution after agitation and incubation for 10 min in the dark.

- **Nitrates**

  In this test, some of the nitrate was reduced to nitrite while stirring in the presence of cadmium grains. A buffer solution of ammonium chloride 0.7 N of pH 8.5 was prepared with 12–50 mesh cadmium, washed with HCl_6N, and rinsed three times with mineralized water. In a 15-mL plastic vial, we added 1 mL of the NH_4Cl buffer solution, 2 g of cadmium, 4 mL of Milli-Q water, and 1.0 mL of the sample and placed the tube horizontally on a stirring table for 2 h, allowing reduction of the nitrate to nitrite. Then, similarly to the nitrite colorimetric method, in a 1-cm spectrophotometric cell at 540 nm, we added 2 mL of sample and 0.150 mL of sulfanilamide solution after agitation and incubation for 10 min in the dark to determine the value of nitrate plus nitrite. To determine the actual value of nitrate, the value of nitrites was subtracted from the sum of nitrite and nitrate (Equation 3.8):

$$NO_3 = (NO_3 + NO_2) - NO_2 \qquad \text{(Equation 3.8)}$$

Other water quality parameters

3.1.3.4. Organic composition of water

The characteristics of sample organic composition were studied through analyzing the online TOC, DOC, UV absorbance (UVA_{254}), and color. In addition, the size distributions of the NOM samples were studied by size-exclusion chromatography (liquid chromatography-organic carbon detection (LC-OCD)), as performed at the University of Waterloo on a Huber system. Except for the TOC, the other samples were collected in carbon-free glassware. Before starting the analysis, filtration with a 0.45-µm filter (Supor 450, PALL) was performed within 24 h. In addition, the impact of the organic composition removal on the potential formation of DBPs, THM, and HAA were determined with capillary column gas chromatography/mass spectrometry.

3.1.3.4.1. Total organic carbon

Total organic carbon indicates the quality of the water and represents the entire available organic carbon contained in the water (both dissolved and particulate carbon). It was monitored online

24/7 in the DWTP using a Sievers 900 on-line TOC analyser, GE Water (Figure 3.4).

Figure 3.4 : TOC online

3.1.3.4.2. Dissolved organic carbon

The samples were filtered as described earlier and held at 4°C for a week. For longer storage, the samples were acidified to pH 2.0 with 2 drops of H_3PO_4 and preserved at 4°C. Samples were measured with a Sievers M5310C Laboratory TOC Analyzer-GE Autosampler.

3.1.3.4.3. UVA254/ true colour

UVA_{254} and colour were measured with a spectrophotometer (Ultrospec 3100 pro – UV/visible Spectrophotometer). After filtering the samples, using a 1-cm path-length cell and a wavelength of 254 nm, the specific light absorbance was determined. In addition, using a 5-cm cell and a wavelength of 456 nm, the true color is calculated using the following conversion: True color = 0.0013 × Absorbance + 0.0045.

3.1.3.4.4. LC-OCD

Liquid chromatography of organic carbon detection (LC-OCD) was performed at the University of Waterloo based on the method applied by Huber et al. (Huber et al., 2011). This analysis required particle-free samples (achieved with 0.45-µm filter). A high-performance liquid chromatography (HPLC) pump passed the phosphate buffer (pH 6.85) to a chromatographic column, where, at the OCD, the samples were acidified with a solution containing 4 mL o-phosphoric acid (85%) and 0.5 g potassium peroxodisulfate in 1 L of mineralized water. The acidification converted carbonates to carbonic acid, which was then stripped. A portion of the

column feed was by-passed to read the DOC value of the entire sample.

3.1.3.4.5. THM- UFC, HAA-UFC

THM and HAA precursors were assessed using the uniform formation conditions (UFC) method proposed by Summers et al. 1996, involving the dosing of sufficient chlorine to maintain a free chlorine residual of 1 mg Cl_2/L after 24 h of contact at pH 8.0 and T = 22°C. The measurement of THM was performed according to USEPA, Method 524.2 (USEPA, 2007) and that of HAA was performed according to USEPA, Method 552.2 (USEPA, 2003) using a gas chromatograph (GC) (Agilent Technologies 7890B).

3.1.3.4.6. Mass balance

In order to distinguish the mechanism of NOM removal by IEX or biodegradation, the accumulated carbon in the resin beads of the IEX and BIEX filters was extracted before BIEX regeneration. With the DOC concentration of the source water and the filter effluent from the entire operation, the total amount of carbon removed by BIEX was determined. The carbon extracted from the BIEX resin beads represented the NOM removal by ion exchange; the difference of this amount from the TOC removed by BIEX indicates the NOM removal by biodegradation (Equation 3.10). The calculation for IEX and BIEX is done as follows:

$$(\text{Total removed carbon})(\text{mg}) = [\text{DOC}_{\text{ave}}]_{\text{SW}}(\text{mg}) - [\text{DOC}_{(\text{effluent})\text{ave}}]_{\text{BIEX/IEX}}(\text{mg}) \quad \text{(Equation 3.9)}$$

$$(\text{Carbon removal by biodegradation})(\text{mg}) = (\text{Total removed carbon})(\text{mg}) - (\text{Extracted carbon from resin})(\text{mg}) \quad \text{(Equation 3.10)}$$

3.1.3.5. Nitrogen analysis

3.1.3.5.1. Ammonia

Before sampling and analysis, all glassware was rinsed with HCl (25%) and ammonium chloride was heated at 100°C for 1 h. A stock-solution of 100 mg/L N-NH_3 was prepared by adding 0.0382 g of NH_4Cl to 100 mL Milli-Q water; a standard curve was made using serial dilutions. Ammonia analysis was performed in two steps. In the first step, a 1-mL solution of phenol/nitroprussiate and 1 mL of alkaline solution were added to 20 mL of the sample. Then, the sample was incubated in the dark for 6 to 24 h. In the second step, the standards and samples were read at 630 nm in 5-cm

spectrophotometric cells.

3.1.3.5.2. Nitrites/ Nitrates

As with the chloride measurement, measuring of nitrites and nitrates was performed according to the analytical method MA. 300 Ions 1.3 of CEAEQ (2014).

3.1.3.5.3. LC-OND

Liquid chromatography of organic nitrogen detection (LC-OND) analysis was performed similarly to LC-OCD analysis (section 3.1.3.4.4), in which another stream with restricted flow was used to read the nitrogen values.

CHAPTER 4 ARTICLE 1 - LONG-TERM PERFORMANCE OF BIOLOGICAL ION EXCHANGE FOR THE REMOVAL OF NATURAL ORGANIC MATTER AND AMMONIA FROM SURFACE WATERS

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Long-Term Performance of Biological Ion Exchange for the Removal of Natural Organic Matter and Ammonia from Surface Waters

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Abstract

Anionic exchange is an effective treatment option for the removal of natural organic matter from surface waters. However, the management of the spent brine regenerant often limits the adoption of this process. The current study reports one year of operation of ion exchange resins under biological mode (BIEX, i.e. without regeneration to promote biofilm growth on the media) compared to the performance of (i) ion exchange with weekly regeneration (IEX), (ii) granular activated carbon under biological mode (BAC) and (ii) granular activated carbon under adsorption mode (GAC). Four parallel pilot filters (GAC, BAC, IEX and BIEX) were fed with a colored and turbid river water without pretreatment. Although IEX provided the best performance (80 % DOC removal) throughout the study, BIEX achieved a similar performance to IEX prior to DOC breakthrough (92 days) and subsequently achieved a mean DOC removal of 62 % in warm water conditions. The GAC filter was rapidly exhausted (2 weeks) while the BAC filter only provided a 5 % DOC reduction. Full nitrification was observed on both the BIEX and BAC filters under warm water conditions (> 15^{o}C). After one year of operation, BIEX was successfully regenerated with brine. According to a mass balance, 69% of DOC removal in BIEX was due to ion exchange while we assume the remainder was biodegraded. Operation of ion exchange in biological mode is a promising option to reduce spent brine production while still achieving high DOC removal.

Keywords: Ion Exchange, Activated Carbon, Biological Mode, Natural Organic Matter, Ammonia, Drinking Water

Highlights

- In the biological IEX filter, DOC breakthrough occurred after 60 days.
- After DOC breakthrough, BIEX reduced DOC from 7 mg C/L to 2-3 mg C/L in warm water.

- Nitrification in warm water was as efficient in BIEX filters as in BAC filters
- BIEX media was successfully regenerated after 331 days of operation.
- NOM removal in BIEX was mostly (69%) due to ion exchange.

4.1. Introduction

Natural Organic Matter (NOM) is ubiquitous in surface waters (Matilainen and Sillanpaa, 2010; Pelekani and Snoeyink, 1999). Adequate NOM removal during drinking water treatment is of importance as the presence of NOM deteriorates water quality and disrupts several water treatment processes. These deleterious NOM impacts are numerous: poor aesthetic water quality such as taste and odours (Christman and Ghassemi, 1966), formation of chlorinated disinfection by-products (DBPs) (Kleiser and Frimmel, 2000; Xie, 2003), potential bacterial regrowth and biofilm formation in distribution systems (Vanderkooij, 1992), reduction of micropollutants sorption on activated carbon (Smith and Weber, 1985), membrane fouling (Amy and Cho, 1999; Nilson and DiGiano, 1996), impact on UV and UV-based advanced oxidation processes (Sarathy et al., 2011), decrease in the rate of oxidation of iron and manganese (Graveland and Heertjes, 1975), etc. Given this long list of negative impacts, it is not surprising that NOM removal has received much attention in the scientific literature.

Available water treatment processes for NOM removal are numerous and include coagulation, high pressure membranes (e.g. NF), sorption-based processes (ion exchange and activated carbon) and biological treatment. For small water systems in remote areas, selecting an appropriate process is challenging as the issues of cost and complexity of operation are important design constraints. Passive and robust systems with low production of residuals are desirable. Biological filtration with activated carbon (BAC) has been considered as an economical and passive option for the removal of dissolved organic carbon (DOC) and DBP precursors. However, DOC removal under steady-state BAC is typically in the low range of 5-20 % (Terry and Summers, 2017). On the other hand, ion exchange (IEX) is a promising robust and simple treatment alternative to remove color, DBP precursors and chlorine demand as typically 85-95 % of NOM is negatively charged (Boyer et al., 2008) and, therefore, potentially removable by IEX. However, spent brine management is an important drawback of this option as severe discharge limits for sodium and/or chloride exist under many environmental regulations in order to protect ecosystems. In addition, regenerant (NaCl) transport to the water treatment facility can be an important constraint for remote

communities such as the ones found in Canada. The development of a robust NOM removal process with low chemical usage, low effluent waste discharge and high performance would clearly represent an important breakthrough for the design of small water systems in remote communities.

As part of RES'EAU-WATERNET, a strategic network dedicated to small water systems, we recently reported the possibility to operate IEX contactors in an extended operation cycle without regeneration (months rather than days), a concept referred to hereafter as biological ion exchange (BIEX) (Schulz et al., 2017; Winter et al., 2018). The lab-scale study of Schulz et al. (2017) compared three abiotic vs. three biotic columns (≈ 2 BV/h, EBCT = 30 min) of Purolite A860 resin. The columns were fed for 2 months (2800 BV) with 0.45 µm pre-filtered surface waters with neutral pH and constant DOC (≈ 5 mg/L) at room temperature (22°C). Three different in-situ regeneration strategies were tested on each biotic and abiotic columns (brine, caustic plus brine or peracetic acid prior to regeneration with caustic and brine). All regeneration strategies were able to fully recover IEX capacity. The presence of biofilm did not impact regeneration efficacy. Biotic columns could remove approximately 60% DOC in contrast to abiotic columns which removed approximately 40% DOC. As a follow-up, Winter et al. (2018) compared the performance of a 3-month acclimatized BIEX with a 5-yr BAC filter using identical test conditions (temperature, EBCT & source waters) to the study of Schulz et al. (2017). Over 11 months of operation (16,000 BV), approximately 56±7% DOC removal was maintained in the BIEX while BAC filtration operating in parallel only provided a 15±5% DOC removal.

Considering the overall cost of salt and brine disposal associated to IEX, it is of interest to increase our understanding of conditions that favor BIEX performance to reduce salt consumption while allowing sufficient NOM removal to meet DBP regulation. Thus, the objective of this study was to investigate the impact of long-term operation of IEX resins without regeneration in order to promote biological activity on the media. For this purpose, we operated pilot columns for a period of 60 weeks. The pilot was directly fed by the Des Prairies River, a source water with high DOC (≈ 7 mg C/L), low alkalinity (≈ 30 mg $CaCO_3$/L) and variable turbidity (5-58 NTU). This long-term operation was performed to confirm the potential viability of BIEX operation mode and its potential superiority against BAC or GAC filtration, even over a long period of operation.

4.2. Materials and methods

4.2.1. Source water characteristics

The pilot plant was located at the Pont-Viau water treatment plant (Laval, Canada) which is fed by the Des Prairies River, a colored and low mineralized surface water (Table 4.1) currently treated at full-scale with a ballasted flocculation, inter-ozonation, biological activated carbon filtration and post-chlorination. During the current study (February 2017 to April 2018), the source water exhibited a significant turbidity (14 NTU), high dissolved organic carbon (DOC) concentration (7.1 mg C/L) and the temperature fluctuated from 1.4 to 23.6°C.

Table 4.1: Source water characteristics of the Des Prairies River (February 2017 to April 2018).

Parameter	Temp. (˚C)	Turbidity (NTU[1])	DOC[2] (mg/L)	TOC[3] (mg/L)	pH	Chloride (mg/L)	Alkalinity (mg $CaCO_3$/L)
Mean ± standard deviation	12.3 ± 7.9	13.9 ± 12.1	7.09 ± 0.34	7.44 ± 0.41	7.2 ± 0.2	5.8 ± 2.6	34 ± 7
Number of samples	39	39	36	24	39	17	42

[1]Nephelometric Turbidity Unit, [2]Dissolved Organic Carbon, [3]Total Organic Carbon. Values are arithmetic averages with standard deviations. Sulfate concentration is typically in the range of 6-10 mg/L.

4.2.2. Experimental set-up and operating conditions

The pilot plant (Figure 4.1) consisted of four parallel filtration columns (PVC, 10 cm diameter and 2 m height) containing 1 m (= 8.1 L) of either (i) ion exchange resins (IEX), (ii) biologically active ion exchange resins (BIEX), (iii) granular activated carbon (GAC) or (iv) biological activated carbon (BAC). The columns were equipped with several sampling taps to allow sample collection at various empty bed contact times (EBCT). The resin type used for IEX and BIEX columns consists of Purolite A860, an anionic strong base resin. The only difference between the IEX and BIEX filter was the frequency of regeneration. Both media were new at the onset of the project. A weekly regeneration of the IEX filter was done by filtering 2 bed volumes (BV) of 120 g NaCl/L whereas the BIEX filter was never regenerated (except for a single regeneration assay performed after about one year of operation). The coal-based activated carbon (AquaCarb® 816, Evoqua, USA) was either fresh (GAC) or exhausted (BAC). The BAC media was collected from the full-

scale filter of the Pont-Viau water treatment plant (WTP) after two years of operation and was therefore considered exhausted.

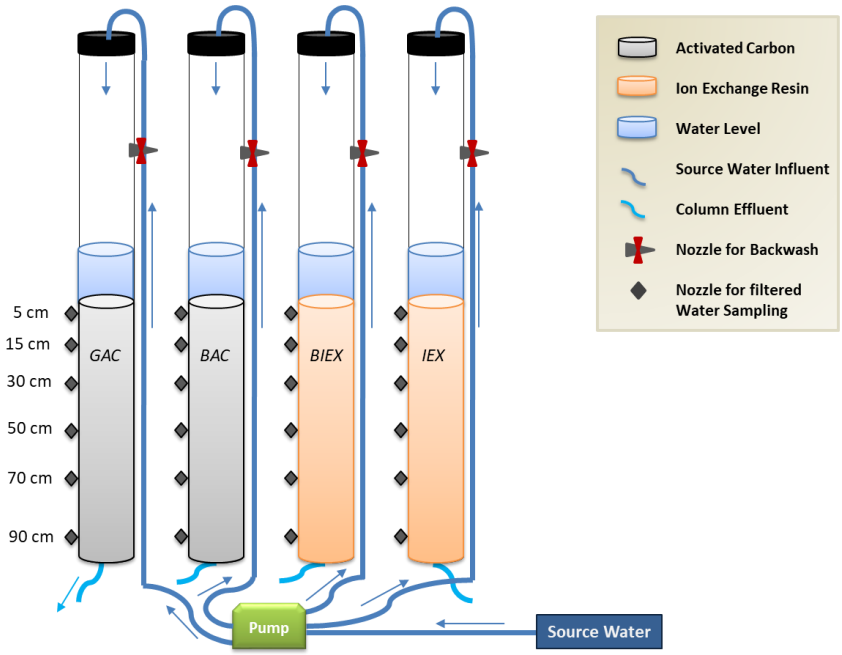

Figure 4.1: Pilot-plant schematic consisting of four downflow filtration columns filled with GAC, BAC, BIEX or IEX filter medium. V = 2 m/h. EBCT = 30 min

The columns were continuously operated at a filtration rate of 2 m/h (2 BV/h or 270 mL/min) which corresponds to an empty bed contact time (EBCT) of 30 min. This filtration rate is lower than commonly used for IEX (5-15 m/h) contactors or BAC filters (10 m/h). This lower velocity was motivated by the fact that (i) the columns were fed by turbid source waters and (ii) the goal was to develop a process which minimizes maintenance. All four filtration columns were backwashed weekly, first using air (2 min at 55 m/h), then water to achieve a media expansion of 50 %. Backwash was continued until the backwash effluent turbidity was < 10 NTU or until 40 L (4 BV) of backwash effluent was collected. The IEX filter was regenerated after performing the backwash.

4.2.3. Monitoring filter performance

Sampling procedures: Influent and effluent streams were monitored weekly for DOC, turbidity, temperature, chloride (Cl^-), trihalomethane (THM), haloacetic acid (HAA) precursors, and ammonia (NH_3). IEX and BIEX anion exchange capacities (AEC) were monitored weekly by

sampling filter media at depths of 5, 15, 50 and 90 cm. Liquid and solid media samples were collected at various depths after 7, 19 and 35 weeks of pilot plant operation (in April, July and November 2017) to assess DOC, NH_3, nitrite (NO_2^-), nitrate (NO_3^-), adenosine triphosphate (ATP), biological nitrifying activity, chloride (Cl^-) and sulfate (SO_4^{2}). In addition, pilot plant performance was compared to the full-scale WTP performance after 19 weeks (July 2017) and 35 weeks of operation (November 2017).

Liquid sample characterization: DOC was quantified according to Standard Method 5310C using a UV/persulfate TOC-meter (Sievers 5310C, GE Water, USA) after filtration through 0.45 µm pore-size filters (Supor® 450 PES, PALL). Turbidity was analyzed using Standard Method 2130B (Standard Methods 2012) using a Hach 2100 turbidy meter. NO_2^-, NO_3^-, Cl^- and SO_4^{2-} were quantified in filtered samples (0.45 µm) by an ion chromatograph (ICS 5000 AS-DP DIONEX) equipped with an AS18 column according to method MA 300 Ions 1.3(CEAEQ, 2014). Bicarbonate was estimated from titration-based alkalinity measurements. THM and HAA precursors were quantified under Uniform Formation Conditions (UFC) (Summers et al., 1996), *i.e.* by maintaining a free chlorine residual of (1.0 ± 0.5) mg Cl_2/L after a contact time of 24 hours at pH 8.0 and 20°C. THM and HAA were analyzed by gas chromatography (7890B GC system from Agilent Technologies) according to methods 524.2 (THM) and 552.3 (HAA) (USEPA 2003). NH_3 was quantified with the indophenol colorimetric method NF T90-015 (AFNOR 2000).

Media sample characterization: Media samples were characterized for nitrifying biomass, total biomass and AEC. Nitrifying bacterial activity was analyzed on filter media according to the method of Kihn et al. (2000). Briefly, media samples (2 cm^3) were collected at various depths with pre-cut sterile plastic syringes. Media samples were washed and then resuspended in a nitrifier medium spiked with 10 mg N/L of NH_4Cl before incubation at 30°C for 30 minutes while maintaining a constant organic-free air sparging. After incubation, formation of NO_2^- and NO_3^- concentrations were measured by colorimetry (Jones, 1984). Potential nitrifying activity is reported as µg N nitrified/cm^3/h.

Total biomass was estimated using ATP measurements performed on detached biofilm from the solid media using 6 cycles of sonication at 20 W on 5 g of media, resuspended after each cycle in 50 mL of sterile phosphate buffer. After each sonication cycle, the supernatant (≈ 50 mL) was recovered and mixed to produce a composite sample which was filtered (mesh size 0.2 micron,

Quench-Gone Syringe Filters, (DIS-SFQG-25), LuminUltra, USA) to retain the bacterial and exclude any extracellular ATP. UltraLyse (LuminUltra, USA) was then filtered to lyse the bacterial ATP retained onto the filter and recover intracellular ATP of detached biomass. After luminase injection in the filtrate, luminescence was read on a TriStar2 Multimode Reader LB 942 (BERTHOLD Technologies). Total biomass is reported as ng ATP/cm^3 of media.

Anion exchange capacity (AEC) of IEX and BIEX resins was monitored by titration. IEX beads (10 mL) were added into 170 mL $NaNO_3$ (25.6 g/L) which was agitated at 190 rpm for another 30 min to displace Cl^- by NO_3^-. The beads were then removed and an aliquot of the filtrate (15-30 mL) was spiked with 1 mL of K_2CrO_4 (20 g/L) and then titrated with $AgNO_3$ (0.04 N) until the solution changed to an orange color due to AgCl precipitation. AEC is expressed as mEq/mL of resin.

4.2.4. Statistical analysis

Significance tests were performed using analyses of variance (ANOVA) with the usual significance level set at $p = 0.05$. Statistical analyses were conducted using Statistica 13.0 (TIBCO Software, USA).

4.3. Results

4.3.1. Evolution of source water temperature

The pilot was started on February 28th, 2017 and was operated for a period of 420 days. The water temperature was less than 2^{o}C until April and progressively increased up to 20^{o}C in June. The water temperature was above 20^{o}C from June to September, before slowly declining to less than 4^{o}C in November. It remained at 4°C for the rest of the project which ended in April 2018. The BIEX column was regenerated in January 31st, 2018 (after 331 days of operation). Following the regeneration of BIEX, pilot performance was monitored for an additional 90 days.

4.3.2. Natural organic matter removal

Source water and effluent DOC concentrations as well as UV absorbance of the four columns operated in parallel were assessed through time (Figure 4.2 and Figure 4.3), while the distribution of DOC measurements prior to BIEX regeneration (331 days) was used to summarize the overall

performance of each media type (Figure 4.4). The source water DOC was fairly stable with an average of 7.1 mg C/L during the study. DOC removal of the BAC filter was marginal (≈ 0.48 mg C/L or 7 %), while the GAC only provided significant removals during the first two weeks of operation. After approximately 200 days of operation, the GAC was fully exhausted and provided the same performance as the BAC ($p > 0.05$). The IEX column offered the highest performance as the effluent DOC in was sustained in the low range of 1-2 mg C/L (*i.e.* an average 80 % DOC removal). The BIEX gave an equivalent performance to IEX for the first 50 days. After this period, the BIEX effluent DOC concentration progressively rose to a maximum of 4.0 mg C/L after 90 days. Interestingly, as the water temperature rose above 15ºC, the BIEX effluent DOC concentration progressively decreased, an indication that biodegradation most likely became a significant DOC removal mechanism. As water temperature declined below 15ºC in fall (after 250 days), the BIEX effluent DOC concentration started to rise again suggesting that a large part of DOC removal during summer may have been due to biological activity. After 331 days of operation (January 23rd, 2018), the BIEX was regenerated and its performance proved to be equivalent to the performance of the IEX column (*i.e.* 1.8-2.0 mg C/L) for the 30 days following BIEX regeneration. Throughout the study, DOC profiles through the filter bed performed after 7, 19 and 35 weeks of operation (Figure S4.11) indicated that most of the DOC removal by BIEX and IEX was achieved in less than 10-15 min of empty bed contact time. Therefore, we suggest that an operation with an EBCT of 15 min should be considered for a BIEX filter design in order to reduce capital costs.

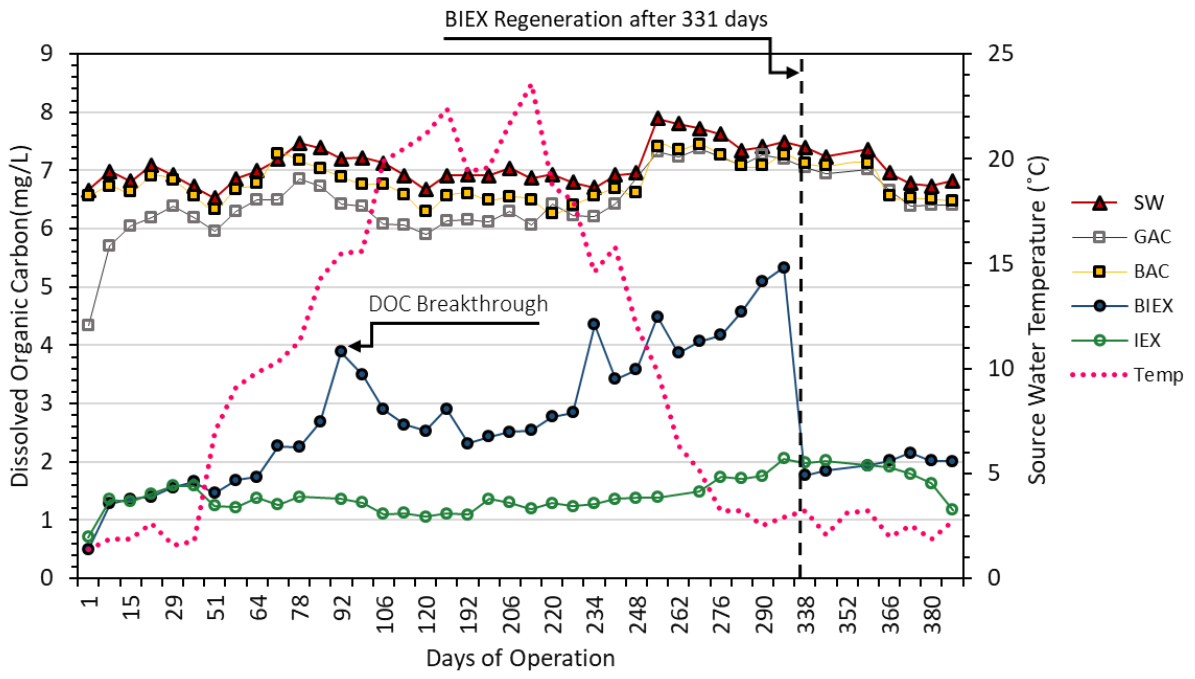

Figure 4.2: Weekly dissolved organic carbon (DOC) monitoring in the source water (SW) and GAC, BAC, BIEX and IEX effluents over a period of 390 days of operation. EBCT = 30 min, V = 2 m/h, 48 BV/d.

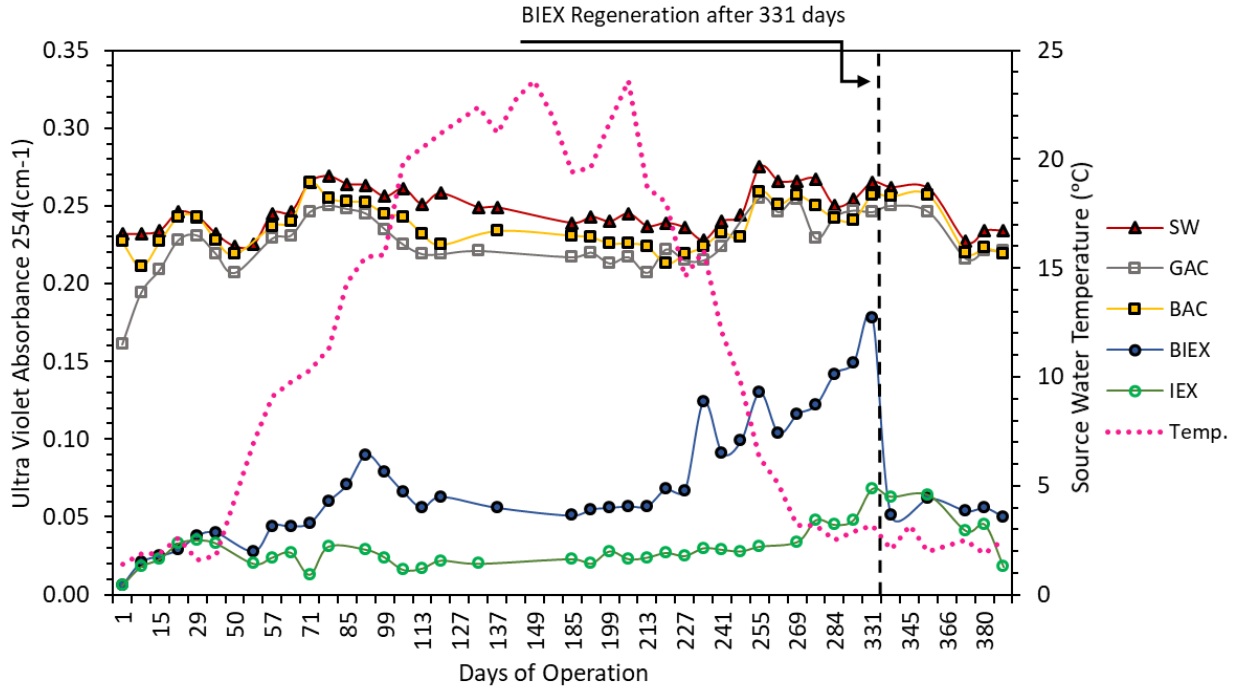

Figure 4.3: Weekly UV absorbance at 254 nm (UVA254) monitoring in the source water (SW) and GAC, BAC, BIEX and IEX effluents over a period of 390 days of operation. EBCT = 30 min, V = 2 m/h, 48 BV/d.

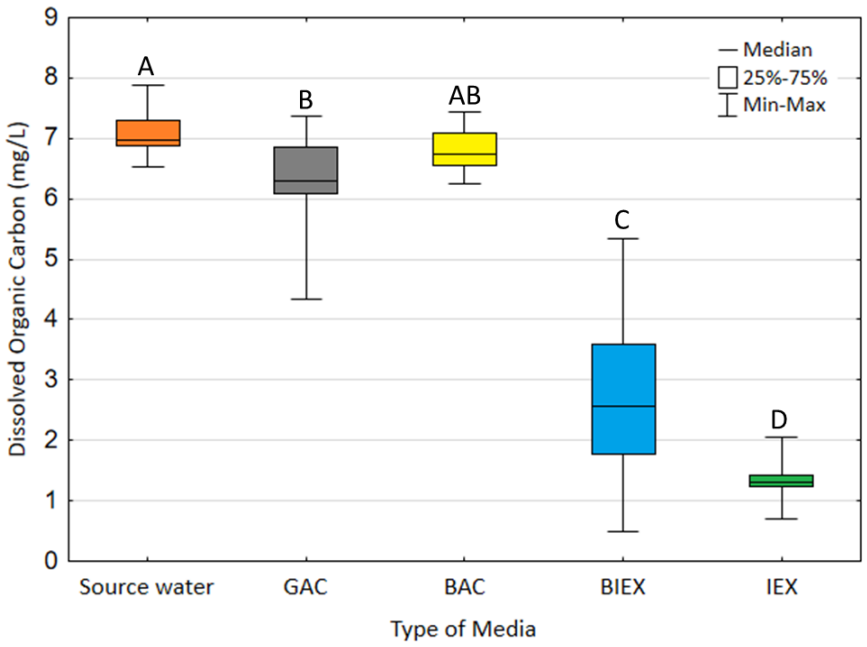

Figure 4.4: Summary of dissolved organic carbon (DOC) concentrations in the source water and the GAC, BAC, BIEX and IEX effluents (n = 36 samples over 338 days, i.e. until the first BIEX regeneration). The groups A, B, C and D were statistically different one from

The impact of temperature on DOC removal was assessed by calculating the activation energies (E_a) for the BAC, the BIEX and the IEX columns. Activation energies can be calculated by plotting a linear regression between ln k vs. $1/T$ where T is the water temperature (in Kelvins) and k is the apparent kinetic constant calculated for each sampling campaign (k was approximated as ΔDOC/EBCT). For the BIEX, only removal data after 100 days of operation were used in order to retain performance under the suspected biological mode. The results (Figure 4.5) indicate that the activation energies are respectively (20 ± 5), (30 ± 4) and (30 ± 8) kJ/mole for the IEX, BIEX and BAC filters. The BAC data should be interpreted with caution due to the very low DOC removals measured for this media (which explains the poorer fit). The BIEX filter was more sensitive to variations in water temperature as opposed to the IEX filter. The activation energies of BAC filters have been reported as 54 kJ/mole in the CHABROL model (calculated using data from Laurent et al. (1999)) or 45 (ozonated waters) and 55 kJ/mole (non-ozonated waters) (calculated using data from Terry and Summers 2017).

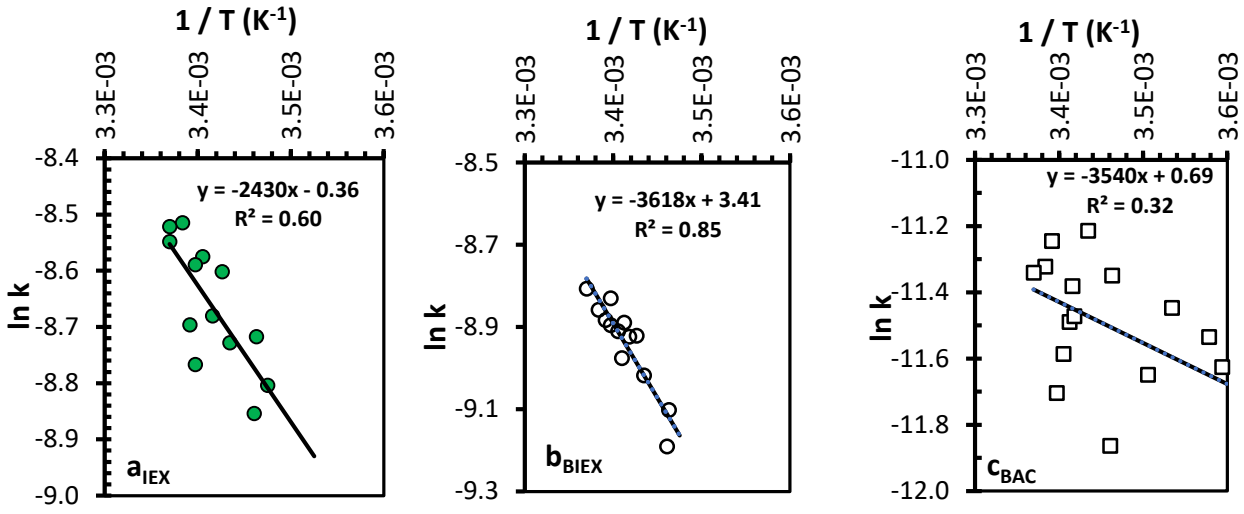

Figure 4.5: Estimation of the energies of activation (temperature effect) for the a. IEX, b. BIEX and c. BAC columns. The slope of the regression line is equal to Ea/R (J/mole). For example, Ea for IEX is given by 2430 x 8.31 = 20 193 J/mole = 20.2 kJ/mole. Ea of IEX and BIEX were calculated with data obtained after 100 days of operation.

4.3.3. Exhaustion of ion exchange capacity

In order to better distinguish the mechanisms responsible for NOM removal, the chloride release in the BIEX and IEX effluents were assessed along with the DOC removal (Figure 4.6). The chloride release from IEX varied from 21 to 34 mg/L from week to week (Figure 4.6-a). The chloride release from the IEX filter was constant and not related to the DOC removal performance (DOC/DOC_0) which was high ($DOC/DOC_0 < 0.25$) throughout the year. In contrast, chloride release from BIEX progressively declined from > 15 mg/L to zero after 90 days (Figure 4.6-b) which coincided exactly with the DOC breakthrough observed in the BIEX effluent. This result suggests that the primary IEX capacity (*i.e.* due to chloride) was exhausted at that time, which corresponds to 4320 bed volumes (BV). However, it is possible that NOM displaced other anions on the media after this period (*e.g.* sulfate or bicarbonate). Finally, BIEX regeneration at 331 days of operation resumed chloride release showing a value similar to IEX at the same period.

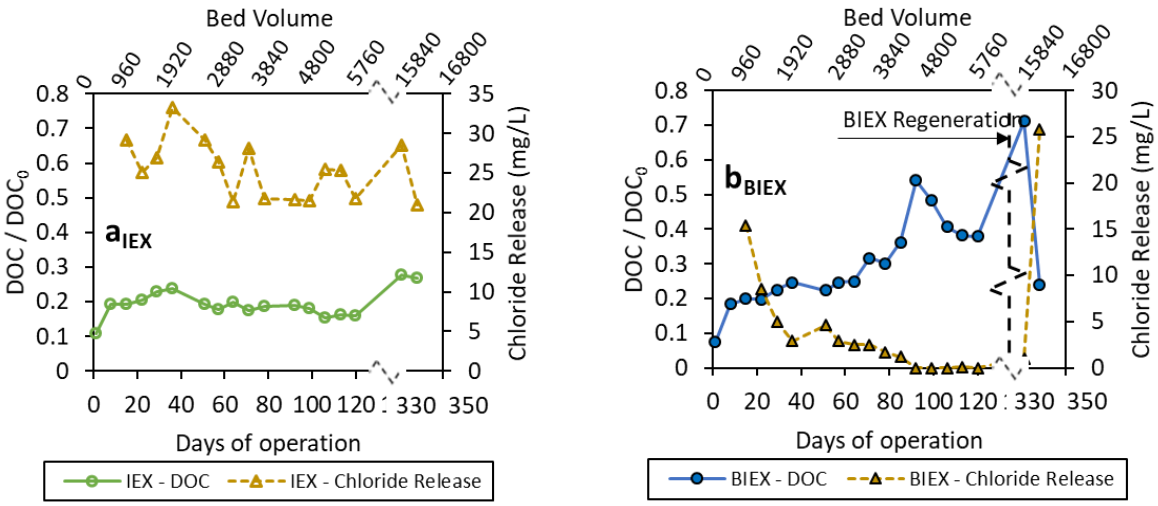

Figure 4.6: Monitoring of ion exchange capacity exhaustion (through chloride release) in parallel with DOC breakthrough in the (a) IEX column and (b) BIEX column. BIEX regeneration occurred at t = 331 days = 15,888 BV.

Ion exchange capacity within BIEX and IEX was also quantified by recovering media from different column depths and measuring the residual IEX capacity (Figure 4.7 and Figure 4.13 for profiles). The IEX capacity for fresh resin was measured in the lab as equal to 0.68 mEq/ml of resin. Results for the IEX filter (Figure 4.7-a) indicates that the weekly regenerations were efficient as the IEX capacities in the middle (50 cm) and bottom (90 cm) of the filter were stable and very high. In contrast, the IEX capacity inside the BIEX declined below 0.1 mEq/mL of resin after 10 weeks of operation. The regeneration after 48 weeks increased the IEX capacity to values similar to that of the IEX at the same period.

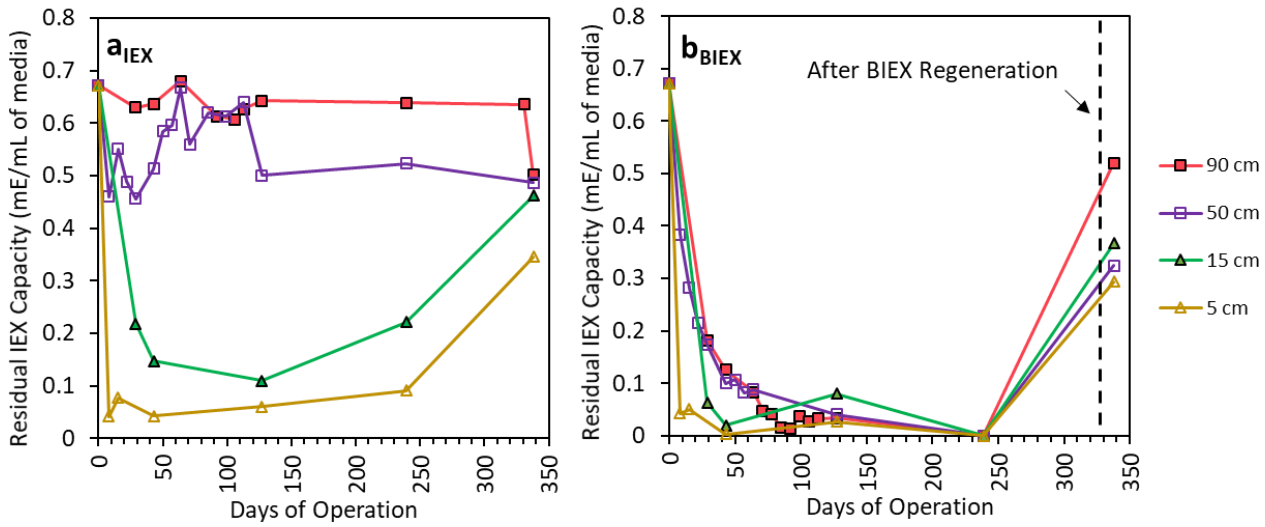

Figure 4.7: Monitoring of ion exchange capacity exhaustion (through chloride release) in parallel with DOC breakthrough in the (a) IEX column and (b) BIEX column. BIEX regeneration occurred at t = 331 days = 15,888 BV.

To understand the mechanism of DOC removal, a carbon mass balance was calculated for BIEX and IEX using the influent/effluent DOC concentrations as well as the DOC measured in the brine recovered after BIEX and IEX regenerations (Table 4.2). Out of the 543 g of carbon removed by BIEX in 331 days, 68.5% was due to ion exchange and the remainder was probably due to biodegradation. As expected, DOC removal in the IEX filter is essentially due to ion exchange (99.4%).

Table 4.2: Organic carbon mass balances in the BIEX and IEX filters

Type of Filter	Influent (g C)	Effluent (g C)	Removal (g C)		
			Total	Mechanisms	
BIEX (After 331 d)	897 g (100%)	354 g (39.5%)	543 g (60.5%)	372 g (68.5%)	Ion exchange[1]
				171 g (31.5%)	Assumed biodegradation
IEX (7 d)	23.1 g (100%)	6.3 g (27%)	16.9 g (73%)	16.8 g (99.4%)	Ion exchange[1]
				0.1 g (0.6%)	Assumed biodegradation

[1]: Based on the DOC measured in the spent brine (18.6 g/L for BIEX and 0.84. g/L for IEX).

4.3.4. Biomass measurement on colonized media

Biomass measurements were performed on the BAC, BIEX and IEX filters after 7 and 19 weeks of operation (April and July 2017). Figures 4.8-a and 4.8-b present the ATP profiles through the depth of the columns for these two sampling campaigns. In general, ATP amounts were higher in the BAC filter, except for the sample at the top of the BIEX filter recovered in April. The biomass density was not a significant predictor of BIEX performance compared to the BAC filter. The average biomasses (based on the profiles) were calculated as (7.0 ± 6.8), (18 ± 18) and (27 ± 11) ng/cm^3 of IEX, BIEX and BAC media, respectively. However, we suspect that ATP measurements were not providing an accurate evaluation of the biomass. We observed that a *schmutzdecke* was developing in the upper portion of the BIEX filter as opposed to the other filters. Breaking down this layer with air injection during the first step of the backwash (BW) was important to properly clean the media during backwash. It was also observed that the BIEX filter required a longer ripening time for turbidity compared to IEX and BAC when the filters were put back in service (see Figure 4.7-c). This excess turbidity most likely results from the biomass sloughing during backwash, as such behavior (*i.e.* long ripening after BW) was not observed on the IEX filter (which was not observed to develop a *schmutzdecke)*. Therefore, ATP measurements may have been inadequate to characterize the biofilm density found in the upper layer of the BIEX filter due to the difficulty to correctly sample the *schmutzdecke*. The average effluent turbidities during the study were 4.0, 5.5, 5.8 and 5.9 NTU for the BIEX, BAC, GAC and IEX filters, respectively. The BIEX filter was therefore providing slightly higher retention of particulate matter, although these filters are not designed for this specific water treatment objective. The BIEX filter also exhibited higher headloss (data not shown: ≈12% higher than IEX) than the other columns.

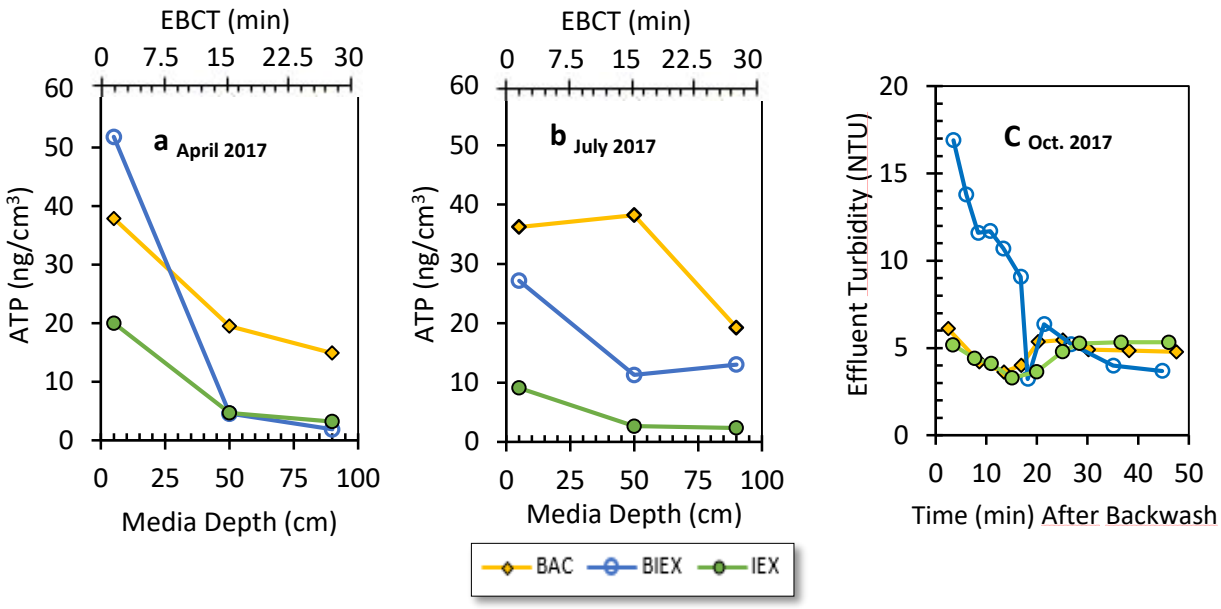

Figure 4.8 Biomass density (ATP) profiles through depth of the BAC, BIEX and IEX after (a) 7 weeks of operation (T= 10oC) and (b) 19 weeks of operation (T=23oC). (c) Typical effluent turbidity ripening after performing a backwash.:

4.3.5. Nitrification

Microbial activity was assessed by monitoring ammonia removal by the columns. Ammonium, a cation, is not expected to be efficiently removed by anion exchange resins. However, nitrate, an anion, is expected to be efficiently removed. For BIEX, it is expected that nitrifying microorganisms will convert ammonia to nitrate which may or may not be removed depending on the degree of exhaustion of the BIEX media. Figures 4.9-a and 4.9-b present the performance of the four media types to remove ammonia during the first 140 days of operation. One last sampling campaign was performed after 340 days at cold temperatures (< 4°C). During the first 50 days of operation, the BAC was the only filter to reduce ammonia below 10 µg N/L as the media was already biologically active at the onset of the study (sampled from the WTP after two years of use). The GAC and BIEX eventually achieved performance equivalent to the BAC filter following an acclimation period of 50 and 78 days, respectively. Throughout the study, the IEX column offered the lowest ammonia removal, an observation suggesting that the weekly brine regeneration was negatively impacting the population of nitrifiers. Nitrate and nitrite profiles were measured across the media after 7 and 35 weeks of operation (Figures 4.9-c and 4.9-d). After 7 weeks of operation, ion exchange was still prevalent within the BIEX as can be noted by the increase of

nitrate in the upper portion of the column. This phenomenon was also observed within the IEX column which evidenced that anion displacement was occurring in these media (Figure 4.9-c). After 35 weeks of operation, ammonia removal was low in the IEX filter while it was close to 100 % in the BAC and BIEX filters. For these two filters, the ammonia was converted into nitrate (Figure 4.9-d), which was not removed by neither BAC nor BIEX, whose IEX capacity had vanished. Only IEX efficiently removed nitrate by ion exchange. At that time, potential nitrifying activity was only detected in the upper media layer (5 cm) of the BAC (1.82 µg N/cm^3/h) and the BIEX filter (4.51 µg N/cm^3/h).

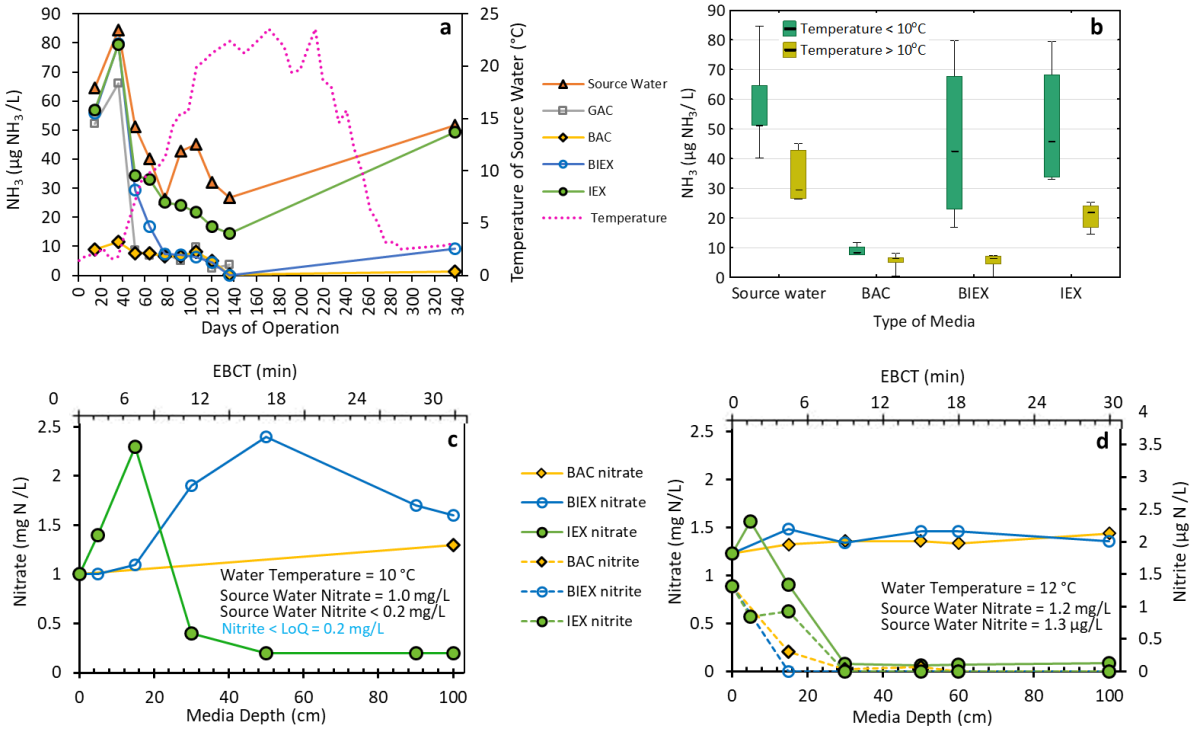

Figure 4.9: Ammonia removal with respect to (a) ammonia through time and (b) impact of temperature on ammonia removal. Nitrate and nitrite formation through depth of the BAC, BIEX and IEX columns after (c) 7 weeks of operation and (d) 35 weeks of operation.

4.3.6. Removal of THM and HAA precursors

The removal of THM and HAA5 precursors was monitored for the first 120 days of operation (Figure 4.10). As expected, the removals were consistent with the effluent DOC concentrations: the IEX filter provided the lowest average THM-UFC (45 µg/L) and HAA5-UFC (41 µg/L) concentrations. The THM and HAA precursors in the BIEX effluent reached a peak at 92 days of

operation, which corresponded to the DOC breakthrough. After this event, the concentrations of THM-UFC and HAA5-UFC declined during the summer to averages of 88 and 51 µg/L, respectively.

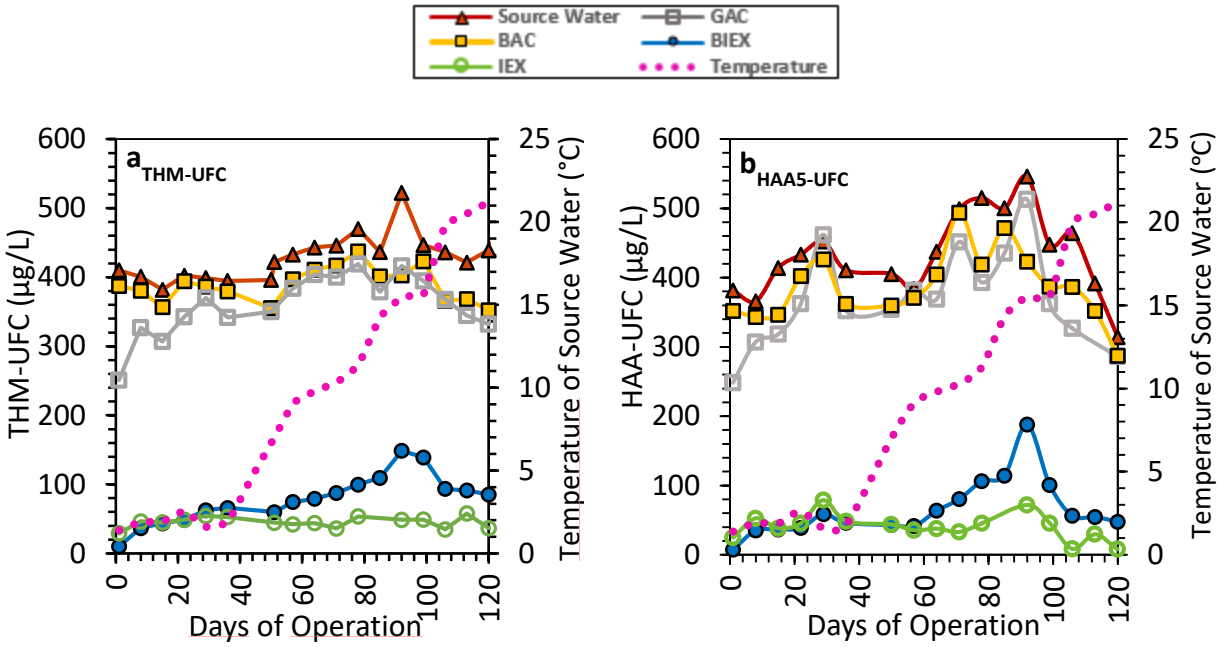

Figure 4.10: THM (a) and HAA (b) precursors concentrations measured under uniform formation conditions (UFC) in source water and in BIEX, IEX, GAC and BAC effluents. Source water temperature: dotted line. EBCT = 30 min.

After 19 weeks of operation (July 2017), a sampling campaign was performed to compare the removal of THM precursors in the IEX, BIEX and BAC effluents as opposed to the unit treatment processes in place at the full-scale WTP (Figure S4.12). Interestingly, the IEX column provided a lower concentration of THM precursors (29 µg/L) than the full-scale plant (35 µg/L) which included ballasted flocculation, inter-ozonation and dual media sand/BAC filtration. In contrast, the performance of the BIEX (72 µg/L) was similar to the effluent from the clarifier (77 µg/L). This was an impressive performance considering that the BIEX column had been in operation for 135 days (6480 BV) without regeneration.

4.4. Discussion

BAC filtration can typically remove 5-20 % of NOM depending on the characteristics of the source water, EBCT and water temperature (Terry and Summers, 2017). The performance of our BAC filter fell within this range. On the contrary, the BIEX filter provided a largely superior

performance. After ion exchange exhaustion of BIEX (based on chloride release), DOC removals as high as 64 % were observed during summer, a performance comparable with the lab-scale pilots that we reported in 2017-2018, fed with a different surface water (5 mg DOC/L) and a 30 min EBCT BIEX filter (Schulz et al., 2017; Winter et al., 2018). The mechanisms responsible for the superior performance of BIEX compared to BAC have not yet been fully elucidated. Theoretical IEX breakthrough was estimated to occur after59 days based on (i) the average sulfate (0.19 mEq) and DOC concentrations (5 mg C/L removed = 0.05 mEq assuming a charge density of 10 mEq/g C at pH 7), (ii) the fresh IEX capacity in the column (5.4 Eq), (iii) the condition of operation (2 BV/h), and (iv) neglecting other anions (bicarbonate & nitrate). Differences in performance of the BIEX and IEX were first observed after 51 days of operation which is consistent with the estimated capacity of the bed. Therefore, we conclude that IEX was not the sole mechanism at play to explain the long-term performance of the BIEX column.

In the studied source water, humic substances compose approximately 75 % of the DOC. To achieve high DOC removal, this NOM fraction, reputed to be very difficult to biodegrade (Catalán et al., 2017), must therefore be partially removed. Using LC-OCD analysis of various surface waters, it has been shown by Catalan et al. (2017) that 20-50 % of aquatic NOM can biodegraded. Our organic carbon mass balance indicates that 31 % of the DOC was probably biodegraded. As anion exchange resins have a superior capacity to sorb NOM compared to GAC, it is speculated that IEX resins offer a more favorable environment for microbial growth than activated carbon. The higher NOM loading present on the media, the high macroporosity of resins and the weak electrostatic bonding of NOM to its surface may favour biodegradation activity, which, in turn, would liberate new sorption sites for additional reaction, as suggested in the concept of bioregeneration (El Gamal et al., 2018). Under such scenario, the BIEX filter would be best described as a process with simultaneous ion exchange and bioregeneration. The organic carbon mass balance indicates that most of the DOC in the BIEX filter (69%) is removed by ion exchange while this value is over 99% for the IEX filter. The activation energy that we calculated for BIEX was also more consistent to an IEX filter than a BAC filter.

Important NOM removal on BIEX was observed after DOC breakthrough even though chloride release from the media was negligible. Apart from biodegradation, secondary ion exchange mechanisms (e.g. displacement of sulfate by NOM) may also be responsible for the long-term

performance of BIEX. Additional investigations will be needed to assess the role of secondary ion exchange on NOM removal. It is anticipated that such phenomenon would be highly source-water specific (i.e. mineralization).

Biomass development on anionic resins is currently considered as a nuisance by resins suppliers. Many suppliers will recommend not to extend regeneration intervals beyond 48-72 h in order to control biomass growth. During this project, we were interested in promoting microbial growth. Heterotrophic and nitrifying biomasses were measured on the BIEX media at amounts that were not largely different from the BAC filter. The measured biomass densities on both media fall in the low range of reported values in the literature for BAC filters (Gibert et al., 2013; Velten et al., 2011; Velten et al., 2007; Zhang et al., 2017). However, the observed formation of a dense and difficult-to-break-up biological layer (*schmutzdecke*) in the upper portion of the BIEX is clearly an issue that will require more attention, given that the low density of anion exchange resins makes the backwashing process more challenging than for other denser granular media.

Biomass is thought to potentially reduce regeneration efficacy. However, in an earlier study, a BIEX filter operated for 60 days (2600 BV) was shown to be effectively regenerated with any of the three different tested strategies of regeneration (brine, caustic plus brine or peracetic acid prior to regeneration with caustic and brine) (Winter et al., 2018). During the present study, the BIEX filter also recovered its ion exchange performance after a regular regeneration following one year (47 weeks) of sustained operation (≈ 15,840 BV). Nevertheless, the resins morphology (color and size) were impacted by this extreme scenario of operation (pictures are provided in Figure S4.14) which also failed to provide the desired effluent water quality (DOC ≤ 2 mg/L) during the entire period. Therefore, the recommended strategy would be to perform the regeneration of the (BIEX) column when breakthrough of DOC is noted in the effluent as opposed to the common strategy based on a very low fixed number of bed volumes. In addition, systems in Nordic climates like Canada would benefit from a regeneration before the cold-water season due to the adverse impact of lower temperature on biodegradation and, to a lower extent, ion exchange. These recommendations would lead to an important reduction in salt usage which will make IEX a more sustainable treatment alternative.

4.5. Conclusion

Four parallel pilot filtration columns were fed with surface water with a high DOC and low mineralization for a one-year period. The IEX column, regenerated weekly, presented the best performance for DOC removal but the lowest for ammonia removal. The BIEX filter provided a largely superior performance to the BAC filter with respect to NOM removal but similar nitrification capacities. The following BIEX performance was noted:

- Effluent DOC concentrations of BIEX were below the treatment goal of ≤ 2 mg C/L for 64 days (≈ 3072 BV), rose to 4.0 mg C/L after breakthrough, stabilized at 2.5 mg C/L in warm water conditions (3072-6768 BV) and finally rose again up to 5.4 mg C/L under winter conditions (< 4ºC). After 141 days of operation (6768 BV), the BIEX was still able to lower TOC from 7.1 to 2.5 mg C/L (October 2017), although its residual anion exchange capacity was below detection.
- The performance for DOC removal of BIEX in warm waters (62 %) was similar to the one observed at lab scale (56 %) in a previous study using a different surface water (Winter et al., 2018). In both cases, BAC performance for DOC removal was significantly lower (5-15 %). THM and HAA precursors were also significantly lower in the BIEX than in the BAC effluent.
- Most DOC removal in the BIEX occurred in the first 15 minutes EBCT. Most of the DOC removal in the BIEX filter (69%) was due to ion exchange.
- After one year of operation, the BIEX column was successfully regenerated.

After ion exchange resin exhaustion, the BIEX column was observed to support heterotrophic biomass. Considering the difficulty to biodegrade humic substances, we speculate that the media is being regenerated biologically. Further studies are ongoing to discriminate the role of biodegradation and ion exchange in the removal of NOM from exhausted ion exchange resins.

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Supplementary information

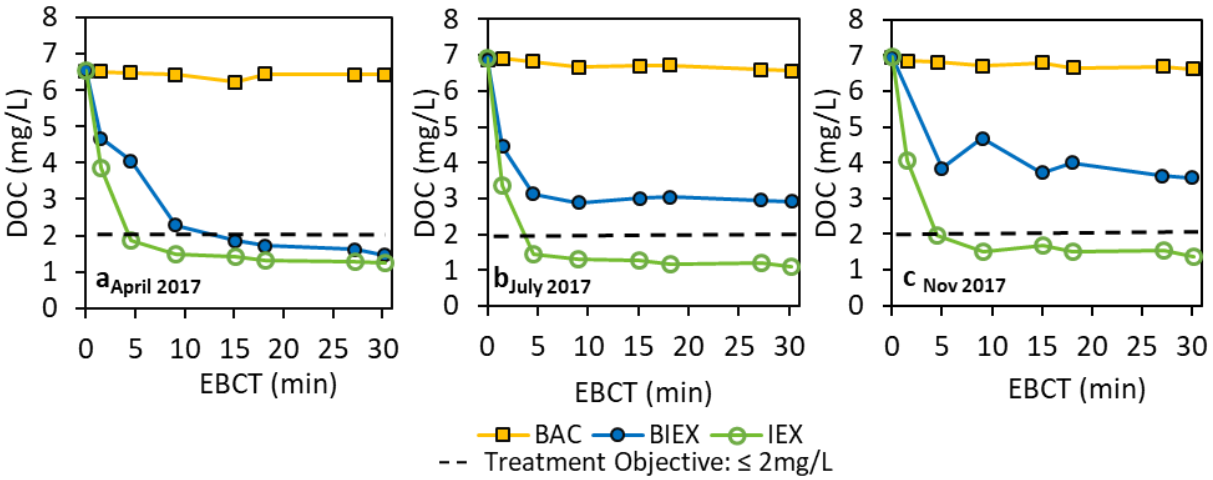

Figure S4.11: Impact of EBCT on DOC removal by BAC, BIEX and IEX after (a) 7 weeks of operation, (b) 19 weeks of operation and (c) 35 weeks of operation

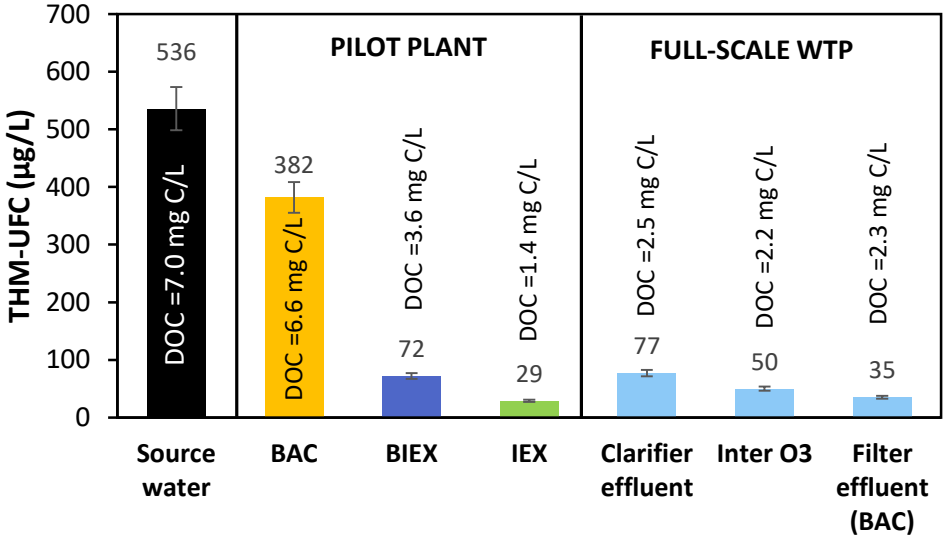

Figure S4.12:THM-UFC in the effluents from the pilot plant (BAC, BIEX, IEX) vs. the full-scale plant (clarifier effluent, ozonation, BAC effluent) after 19 weeks of operation (July 2017).

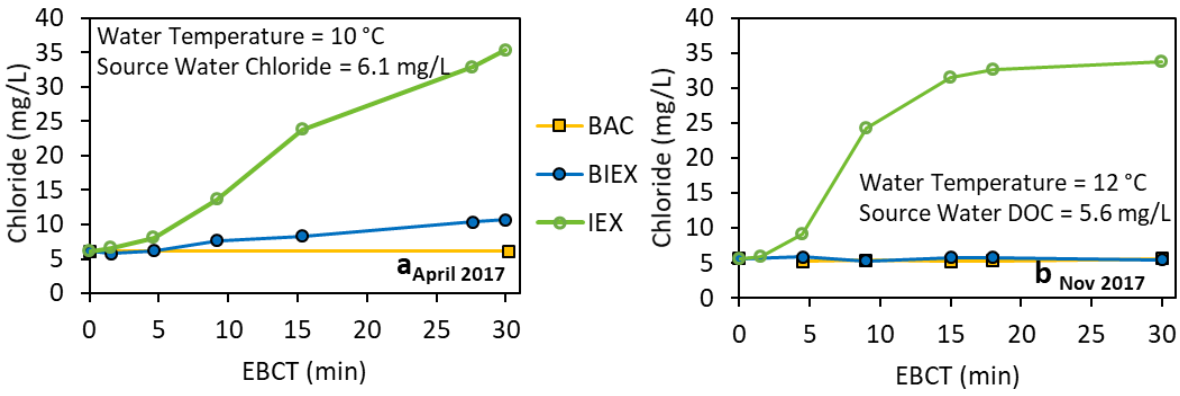

Figure 4.13: Chloride release by BAC, BIEX and IEX as a function of EBCT after (a) 7 weeks or (b) 35 weeks of operation.

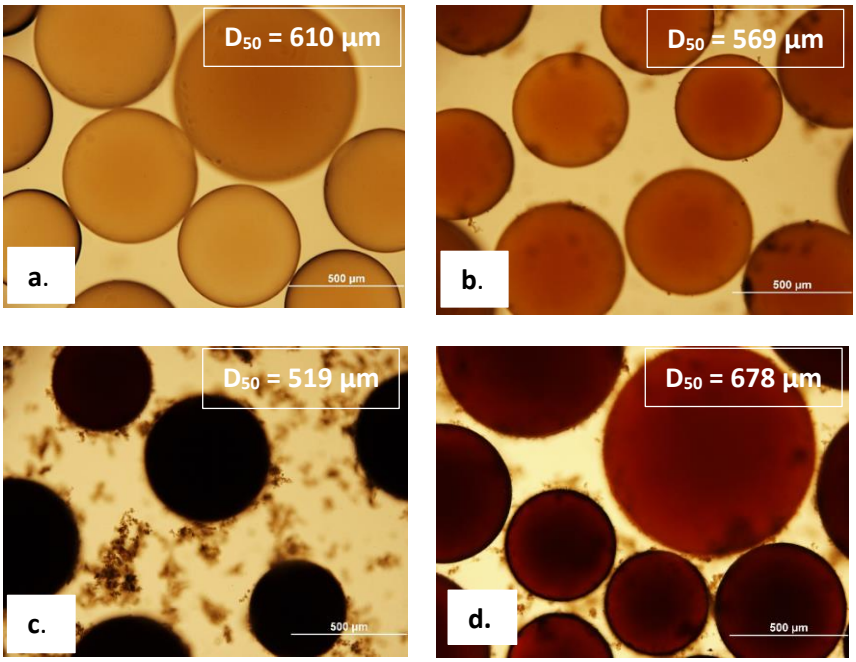

Figure S4.14: Resin morphology for (a) Unused IEX, (b) IEX used for one year, (c) BIEX used for 331 days before regeneration, and (d) BIEX used for 331 days after regeneration.

CHAPTER 5 SUPPLEMENTARY RESULTS

This chapter presents additional results that were not included in the published paper in Journal of Water Research (Chapter 4).

5.1. Evolution of source water characteristics during seasonal changes

The experiment began at pilot-scale operation on February 28th, 2017, and was continued for 442 days, ending on May 15th, 2018. The water temperature was <2°C until April and then progressively increased to 20°C in June 2017. The water temperature was >20°C from June to September, before slowly declining to <4°C in November. The BIEX column was regenerated on January 23rd, 2018 (after 331 days of operation). Following the regeneration of the BIEX column, the pilot performance was monitored for an additional 111 days in which it experienced a temperature increase to 12.4°C (Figure 5.1). Temperature changes affected the column performances in DOC removal (5.2) and nitrification (5.6), specifically for the BIEX column.

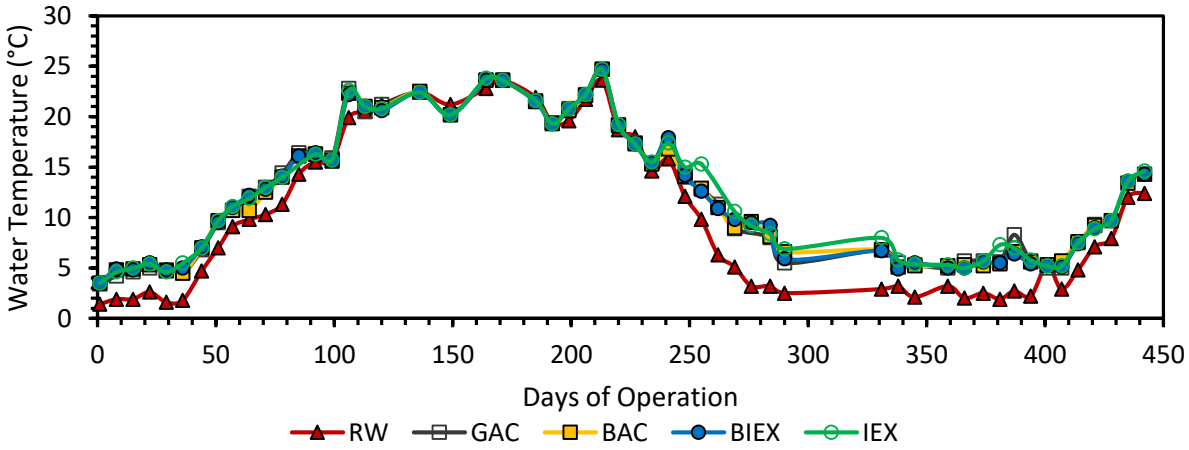

Figure 5.1: Water temperature profiles during the study (°C)

The turbidity of source water exceeded 55 NTU during the pilot operation on April 2017 and April 2018 because of snowmelt. The column performances were not impacted by fluctuations of turbidity (5.2, Figure 5.4). The effluent turbidities of the four columns were slightly different (Table 5.1, Figure 5.2).

Table 5.1: Turbidity through 442 days of operation

	Source Water	GAC	BAC	BIEX	IEX
Number of samples	53	49	53	53	51
Max	58	34	35	31	33
Min	3.13	1.36	1.45	0.7	0.89
Average	14.27	6.77	6.86	5.5	7.49

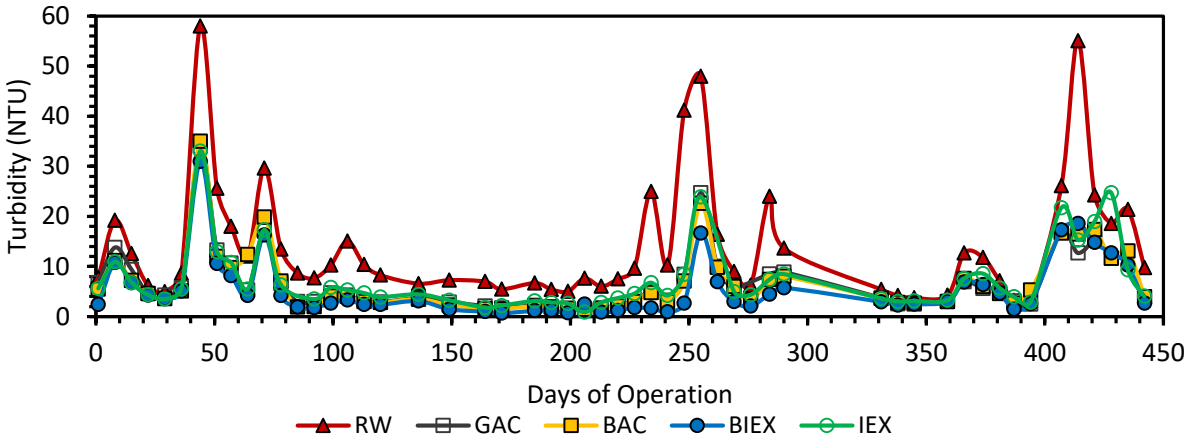

Figure 5.2: Turbidity

The source water remained within the neutral pH range, as did the GAC and BAC effluent. Because of bicarbonate removal by the IEX mechanism, the IEX effluent was acidic (Figure 5.3).

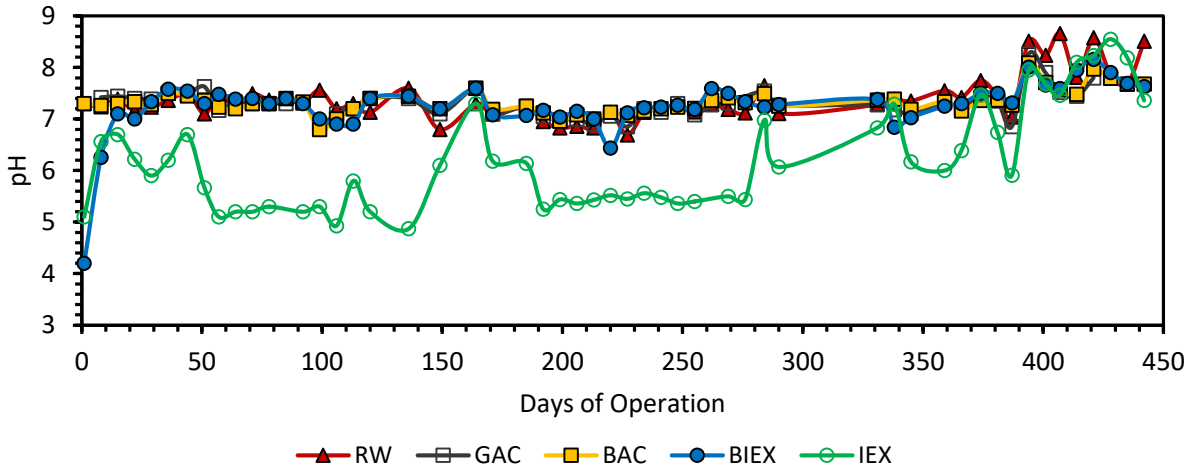

Figure 5.3: Acidity (pH) in source water and filtered effluents

5.2. Natural organic matter removal

The source water and effluent DOC concentrations of the four columns were monitored throughout the study in conjunction with the effects of source water turbidity (Figure 5.4) and temperature (Figure 5.5). Fluctuations of source water turbidity did not affect DOC removal, but the source water temperature had a major effect on the BIEX column performance.

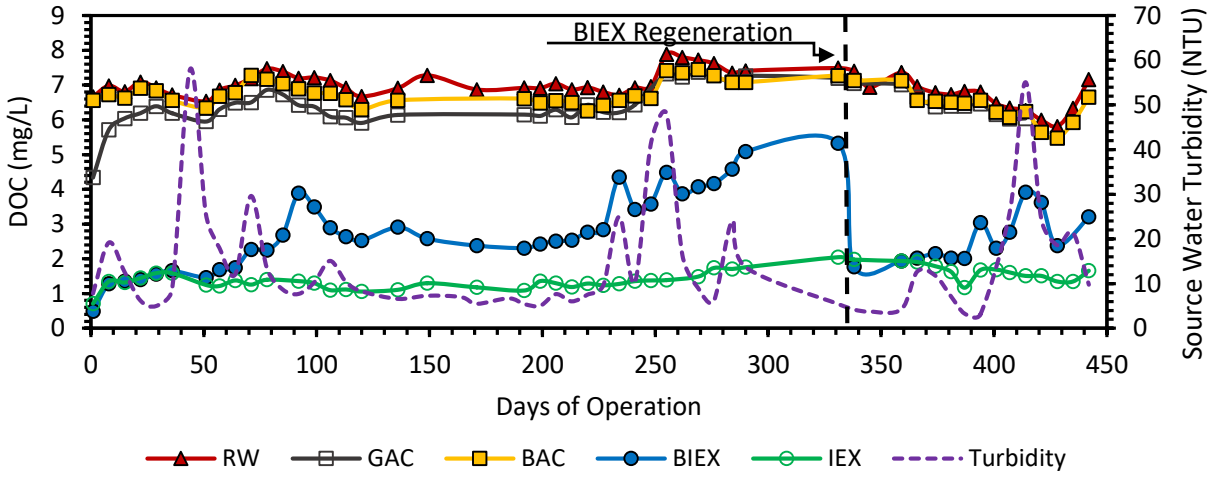

Figure 5.4: DOC removal and turbidity during the pilot study

The distribution of DOC concentrations before BIEX regeneration (331 days) and afterward were used to summarize the overall performance of each media type (Figure 5.6). The source water DOC was stable with an average of 7.1 mg C/L during the study. The GAC column showed significant DOC removal in the first two weeks of operation and reached the exhaustion level after 200 days of operation, performing similarly to the BAC filter. The BAC column exhibited slight DOC removal (≈ 0.30 mg C/L, 4.3%). As expected, the IEX filter provided the highest DOC removal and preserved an effluent DOC meeting the treatment objectives (≈ 1.43 mg C/L, equivalent to ~80% DOC removal).

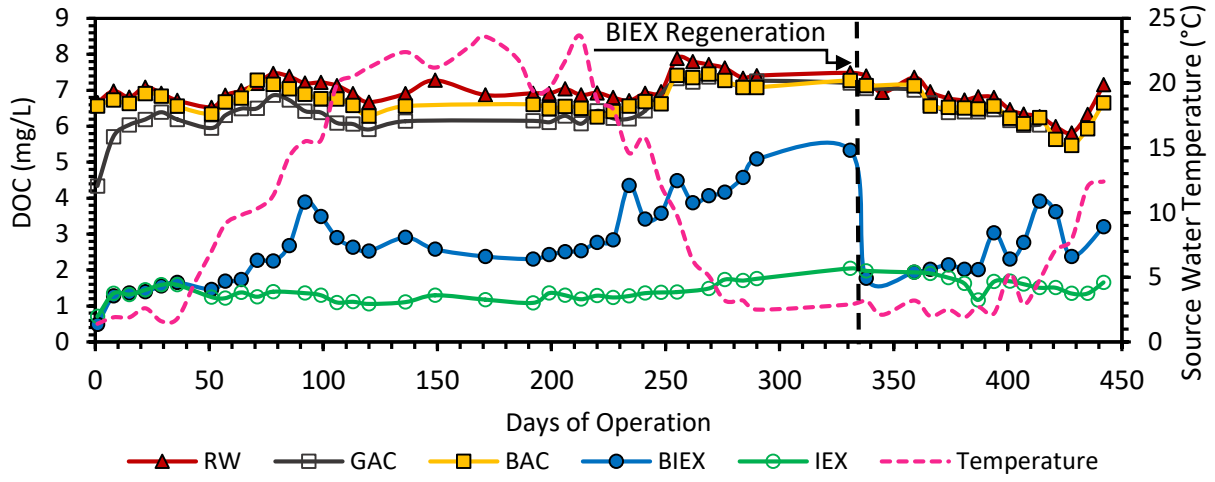

Figure 5.5: DOC removal and temperature

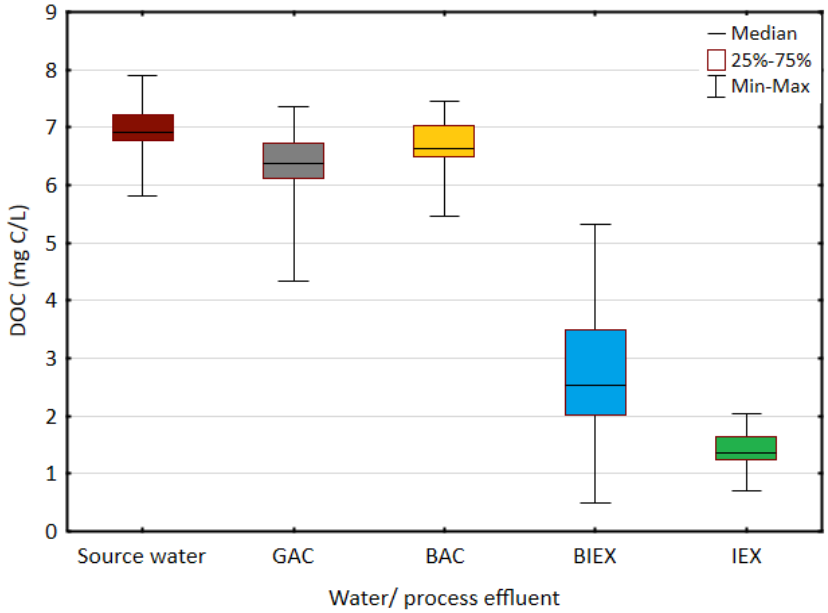

Figure 5.6: [DOC] distribution during 442 days of operation

The BIEX filter underwent various functional modes (Figure 5.7). For the first 51 days of operation, BIEX operated in the ion-exchange mode, like the IEX column, with the effluent DOC of ~1.34 mg C/L. Gradually, BIEX was exhausted and DOC breakthrough occurred on day 92 (3.89 mg C/L). Following the increase in source water temperature above 15°C in the summer, the BIEX effluent DOC decreased to the minimum of 2.31 mg C/L. The IEX capacity and chloride release of BIEX during this stage (section 5.4) supports the hypothesis that the major DOC removal mechanism was biodegradation in this period. Subsequently, the water temperature decreased to

15°C in the fall (after 248 days), and the BIEX effluent DOC began increasing again. The BIEX filter was regenerated after 331 days of operation on January 23rd, 2018. The DOC concentration of the BIEX effluent the week afterward was equal to that of the IEX column. The BIEX column followed the same operation pattern after regeneration as when the pilot operation was started. The distribution of DOC measurements of the BIEX effluent with regard to its various functional modes was used to summarize the performance of the BIEX filter (Figure 5.8).

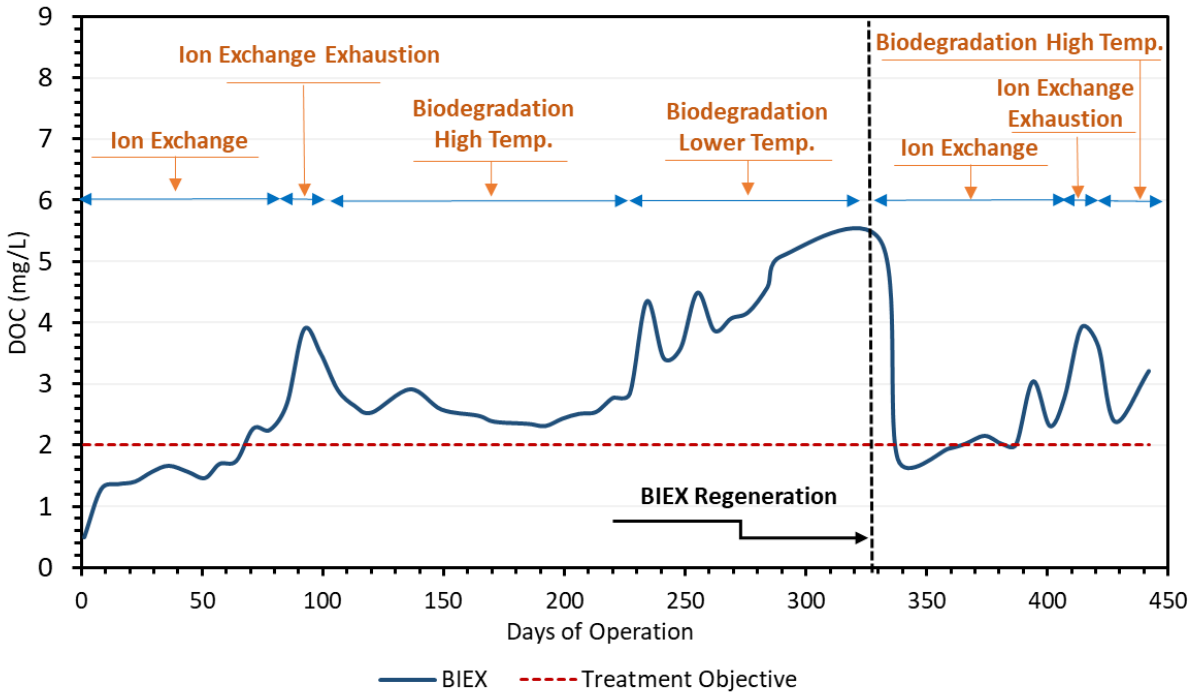

Figure 5.7: BIEX functional mode

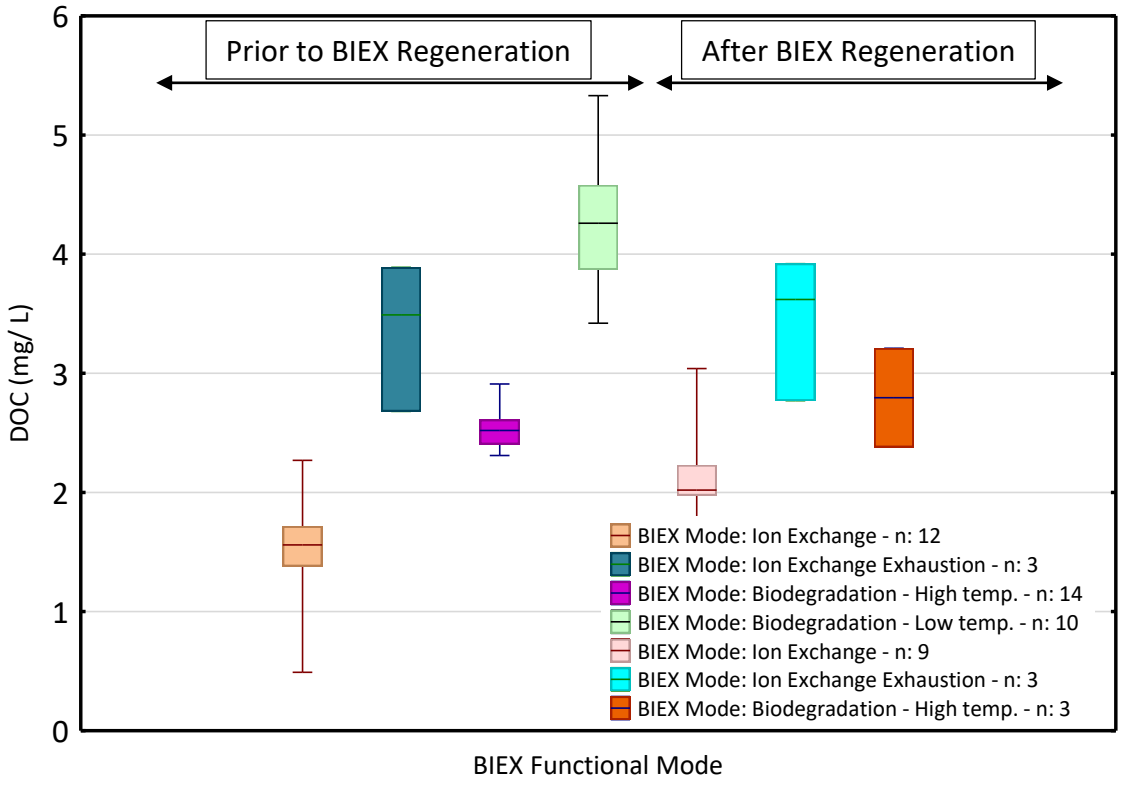

Figure 5.8: [DOC] distribution of BIEX filtered waters during functional modes of operation

Based on the kinetic study of DOC concentration within the filter after 7, 19, 35, and 48 weeks of operation, the most DOC was removed in 10–15 min of EBCT (equal to depths of 33.3–50 cm) for the IEX and BIEX columns (Figure 5.9). This observation suggests considering ~15 min EBCT for column design.

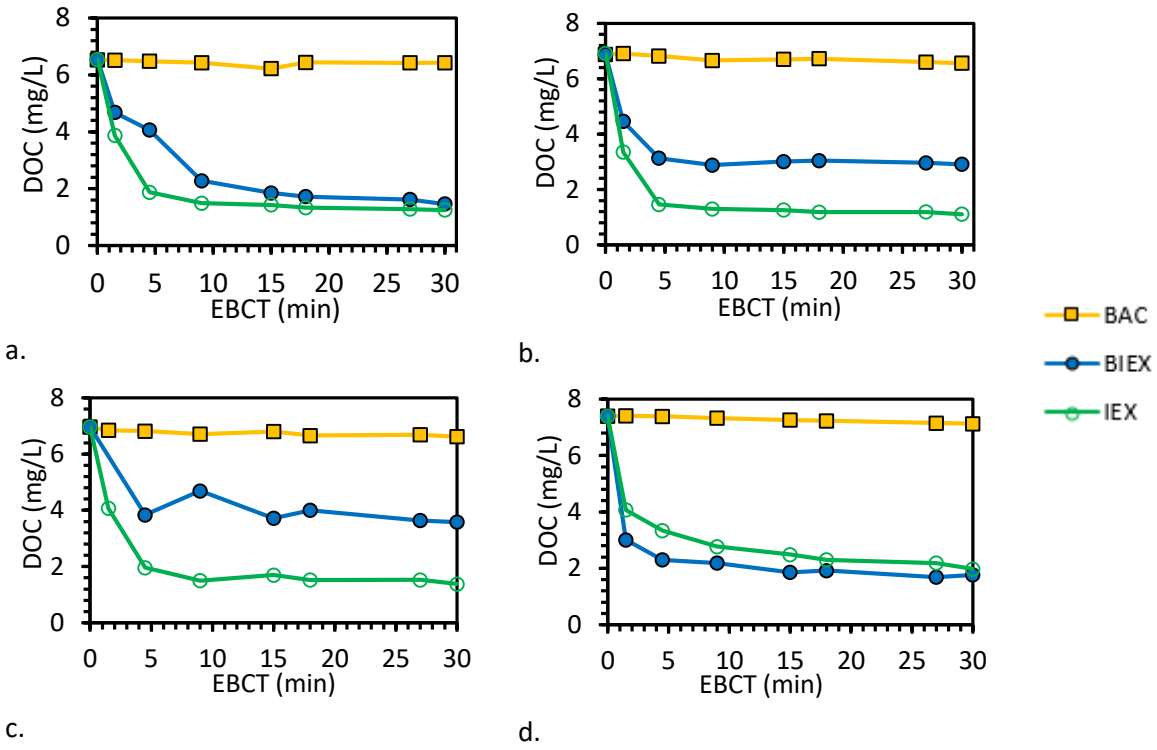

Figure 5.9: Impact of EBCT on DOC removal after, (a) 7 weeks of operation, (b) 19 weeks of operation, (c) 35 weeks of operation, (d) 48 weeks of operation

Due to the difference of activated carbon and anion exchange characteristics, which reflect NOM removal, the removed fraction was studied through size-exclusive chromatography with OCD (Figure 5.10). All four pilot filters removed LMW acids and biopolymers partially and equally; unlike those in the GAC and BAC effluents, humic substances and building blocks and LMW neutrals were removed efficiently only from the IEX effluent. The BIEX filter removed the same NOM fractions as the IEX filter before DOC breakthrough occurred (data is presented for LC-OCD in July).

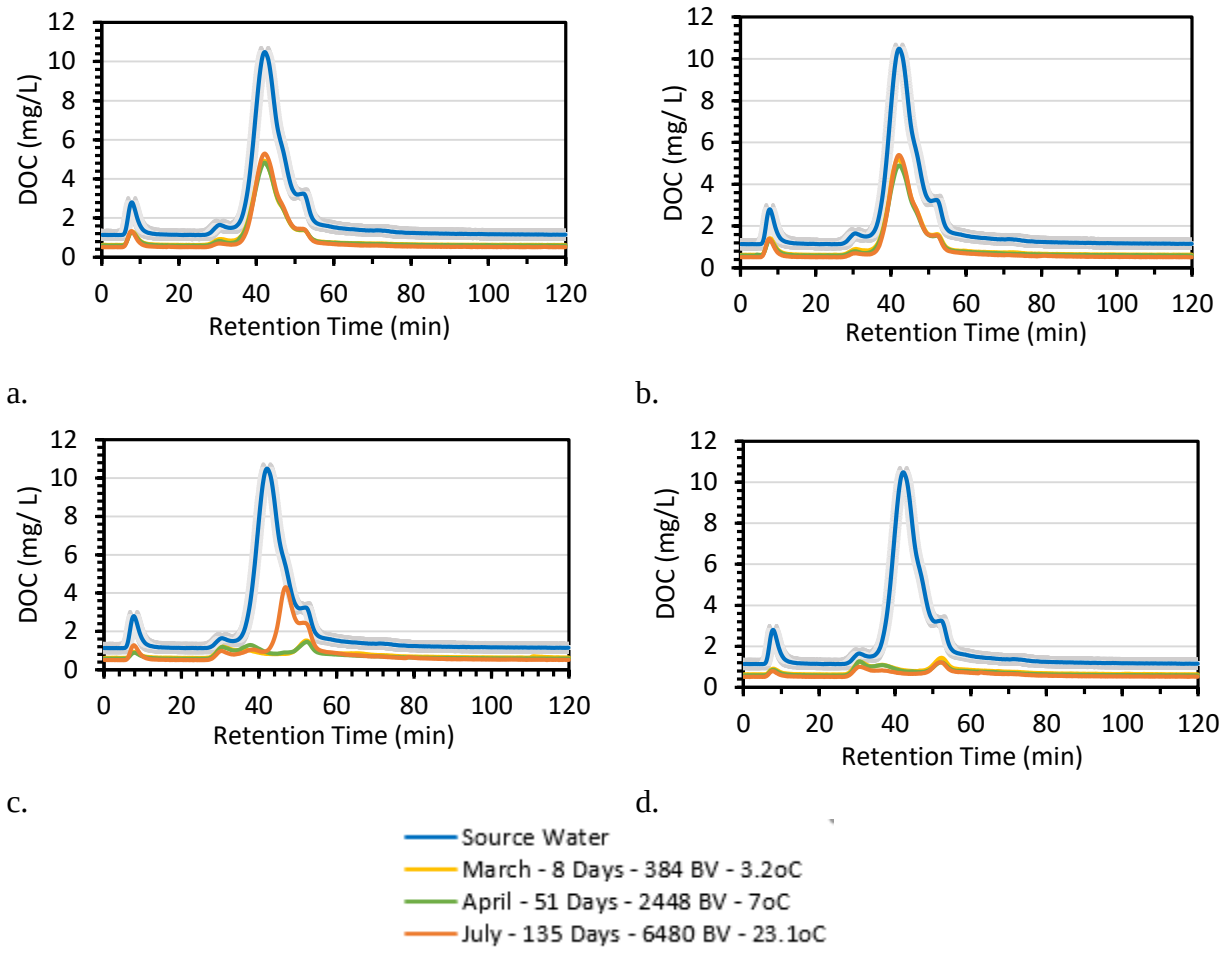

Figure 5.10: Liquid chromatography with organic carbon detection (LC-OCD) for (a) GAC, (b) BAC, (c) BIEX and (d) IEX in March, April, July, 2017 - Source water: The average of three source water measurements in March, April and July

5.3. Removal of THM and HAA precursors

The concentrations of THM and HAA precursors were monitored for the first 130 days of operation and after BIEX regeneration at day 338 (Figure 5.11 and Figure 5.12). As expected, the removals were consistent with the effluent DOC concentrations: THM-UFC and HAA-UFC removals by the GAC and BAC columns were marginal (THM-UFC: ~17% and 10%, HAA-UFC: ~15% and 10%, respectively). The IEX provided the lowest average THM-UFC (45 µg/L) and HAA5-UFC (41 µg/L) concentrations (~90% and 91% removal, respectively). The THM and HAA precursors in the BIEX effluent peaked at 90 days of operation, corresponding to the DOC breakthrough. After this event, the concentrations of THM-UFC and HAA-UFC declined in the summer to averages of 88 and 51 µg/L, respectively. After regenerating the BIEX filter, it resumed

performing similarly to the IEX filter in removing THM-UFC and HAA-UFC.

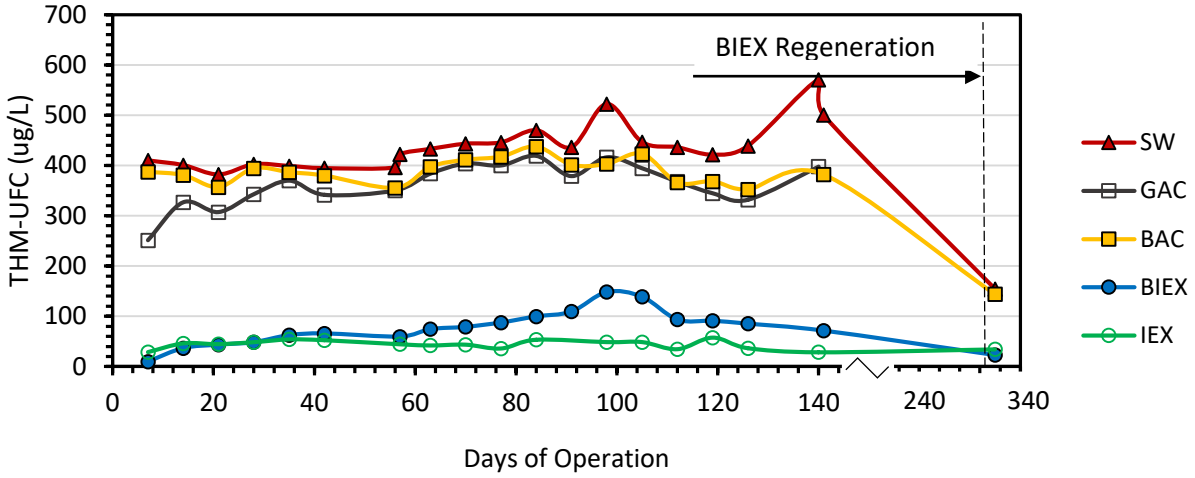

Figure 5.11: THM-UFC concentration of source water and filter effluents

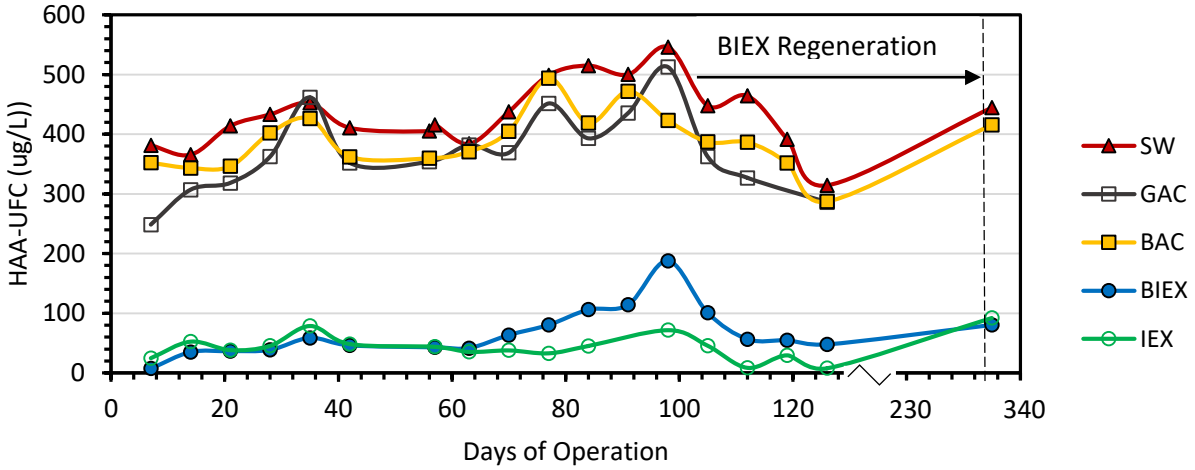

Figure 5.12: HAA-UFC concentration of source water and filter effluents

5.4. Exhaustion of ion exchange capacity

In order to investigate the mechanism of BIEX performance supporting NOM removal, the AEC was sampled (solid) weekly at specific column depth levels for the IEX and BIEX filters. In parallel, the chloride concentrations of the source water and effluents of the IEX and the BIEX were monitored to verify the accuracy of the resin capacity values (Figure 5.13). The resin capacity of the IEX filter remained almost constant throughout the study (~0.6 mEq/mL of resin), while the chloride release varied between 19.7 and 35.5 mg/L. On the other hand, the resin capacity of the

BIEX filter decreased gradually to complete exhaustion (0.01 mEq/mL of resin), while the chloride release decreased from 15.4 mg/L to 0 in 90 days after operation began (corresponding to the DOC breakthrough). After BIEX regeneration at day 331, the resin capacity was entirely recovered in addition to a chloride release elevation (25.8 mg/ L). Interestingly, the resin capacity and chloride release of BIEX filter underwent similar patterns as observed in the beginning of the BIEX filter operation until thorough exhaustion.

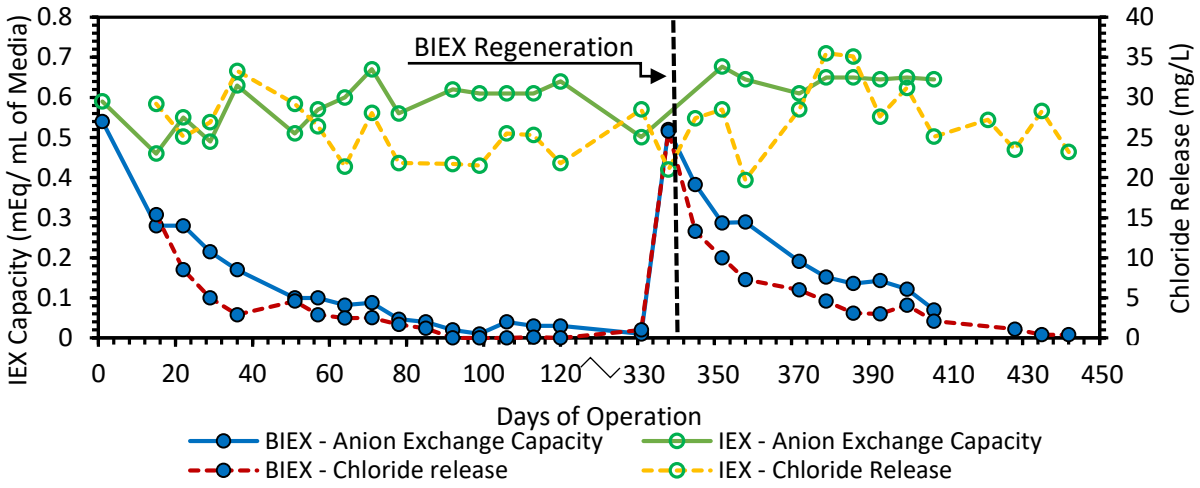

Figure 5.13: Evidence of resin exhaustion in parallel to chloride release

The chloride release was assessed in profile after 7, 35, and 48 weeks of operation (Figure 5.14). Chloride release at week 7 (day 50) showed that BIEX was nearly exhausted at the top; the slight release of chloride release indicated partial NOM removal through the IEX mechanism (Figure 5.14-a). After 35 weeks of operation (day 247), the BIEX was thoroughly exhausted, supporting the hypothesis that DOC removal was due to biodegradation (Figure 5.14-b). Chloride release after BIEX regeneration was approximately equal at equal column depths for the IEX and BIEX filters, indicating the positive recovery of the BIEX resin capacity (Figure 5.14-c).

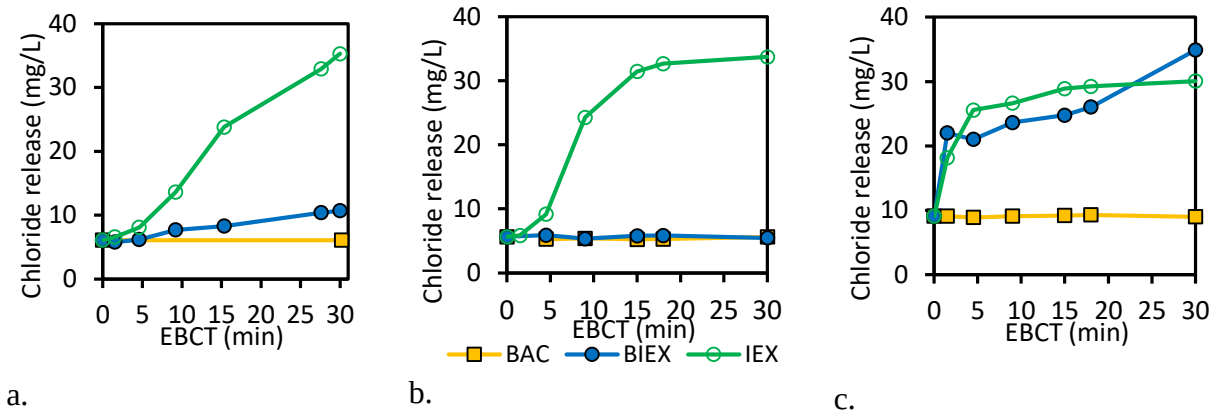

Figure 5.14: Impact of EBCT on chloride release after, (a) 7 weeks of operation, (b) 35 weeks of operation, (c) 48 weeks of operation

5.5. Biomass measurement on colonized media

As previously mentioned in section 4.3.4, the biomass was measured by monitoring ATP for the first 141 days of operation and again after BIEX regeneration (Figure 5.15).

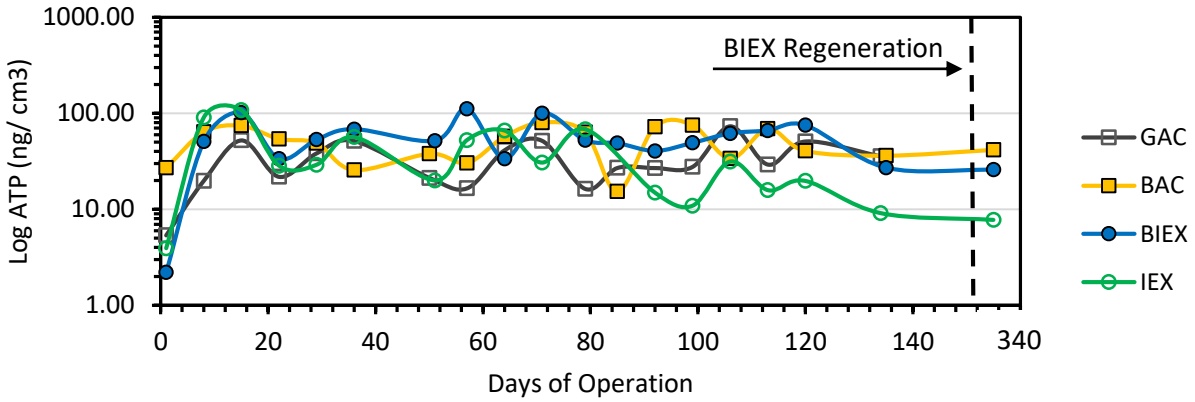

Figure 5.15: Biomass assessment through ATP

5.6. Nitrification

The media performance for ammonia removal was investigated for the first 162 days of operation and again after BIEX regeneration (Figure 5.16). As expected, the IEX filter was unable to remove ammonia because of the positive charge of ammonia, while nitrites and nitrates were efficiently removed in 5–10 min of EBCT (Figure 5.17). As discussed in section 4.3.5, BAC was the only medium with the ability to remove ammonia throughout the study period. GAC showed ammonia removal equal to BAC after it reached exhaustion. With the increase of temperature and nitrifying

bacteria activity in the BIEX column, the BIEX medium started to remove ammonia until reaching full removal after 162 days of operation at the temperature of 14.8°C. During this period, ammonia was completely converted to nitrates in the BAC and BIEX columns (Figure 5.17-b).

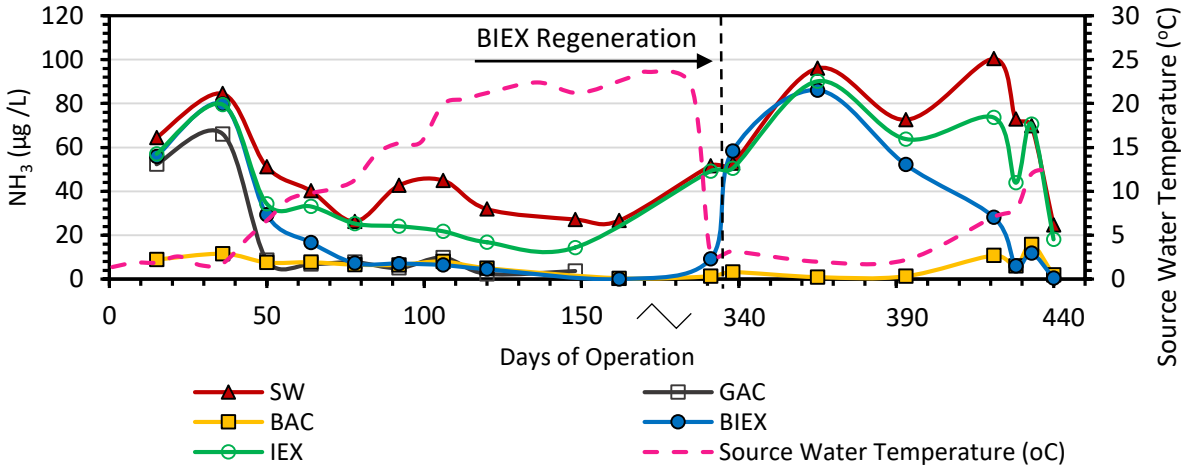

Figure 5.16: Ammonia concentration through time with respect to source water temperature

Regenerating the BIEX filter after 331 days of operation negatively impacted the nitrifying bacteria and rendered the BIEX filter incapable of converting ammonia to nitrate (Figure 5.17-c). In order to guarantee the BIEX performance repeatability, the BIEX behavior was studied after regeneration until it reached the optimum behavior in ammonia removal (100%) at day 442 (Figure 5.16).

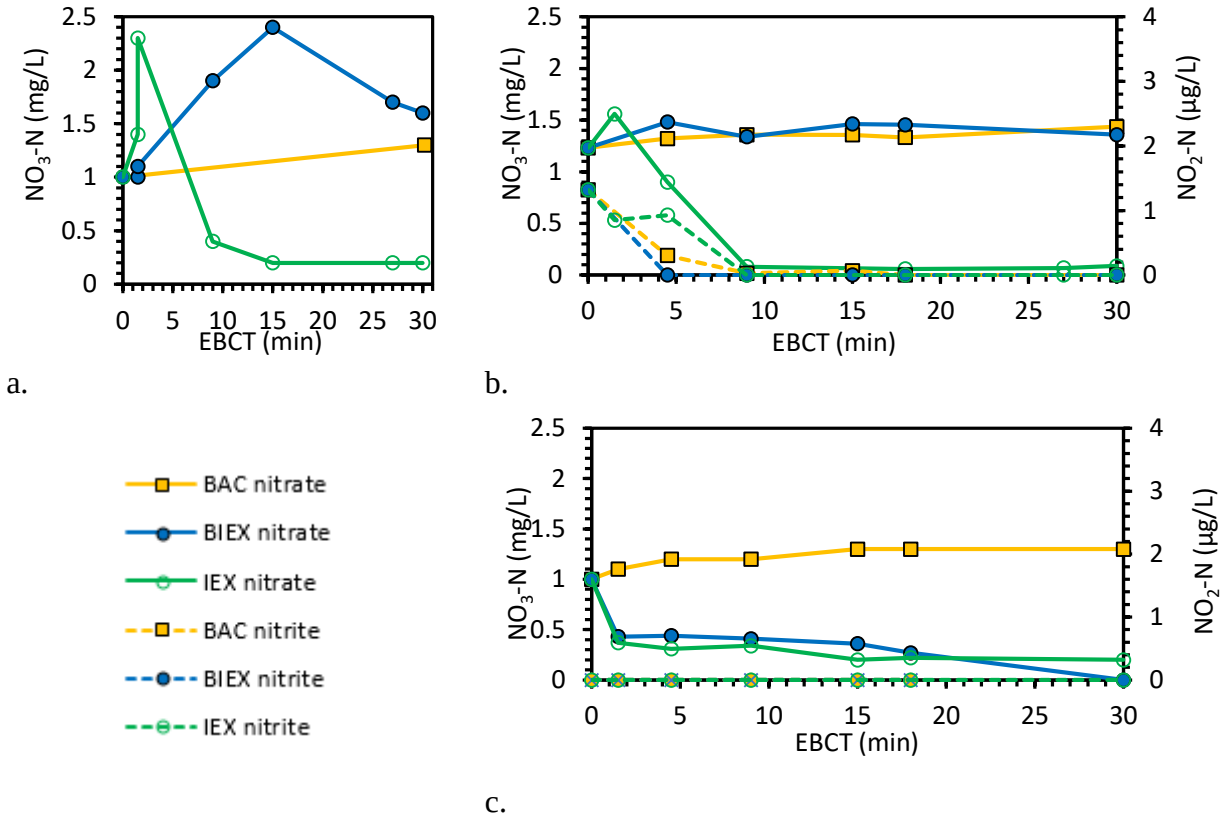

Figure 5.17: Impact of EBCT on nitrate and nitrite removal after, (a) 7 weeks of operation, (b) 35 weeks of operation, (c) 48 weeks of operation

Size-exclusion with OND was used to assess the nitrate and ammonia concentrations in the four columns in March, April, and July 2017 (Figure 5.18). The highest peak indicates nitrate removal (sum of nitrate converted from ammonia and/or as part of source water characteristic). Figures 5.18-a, 5.18-b and 5.18-c show the high concentrations of nitrates in GAC, BAC, and BIEX, respectively, while nitrate is almost completely removed by the IEX filter (Figure 5.18-d).

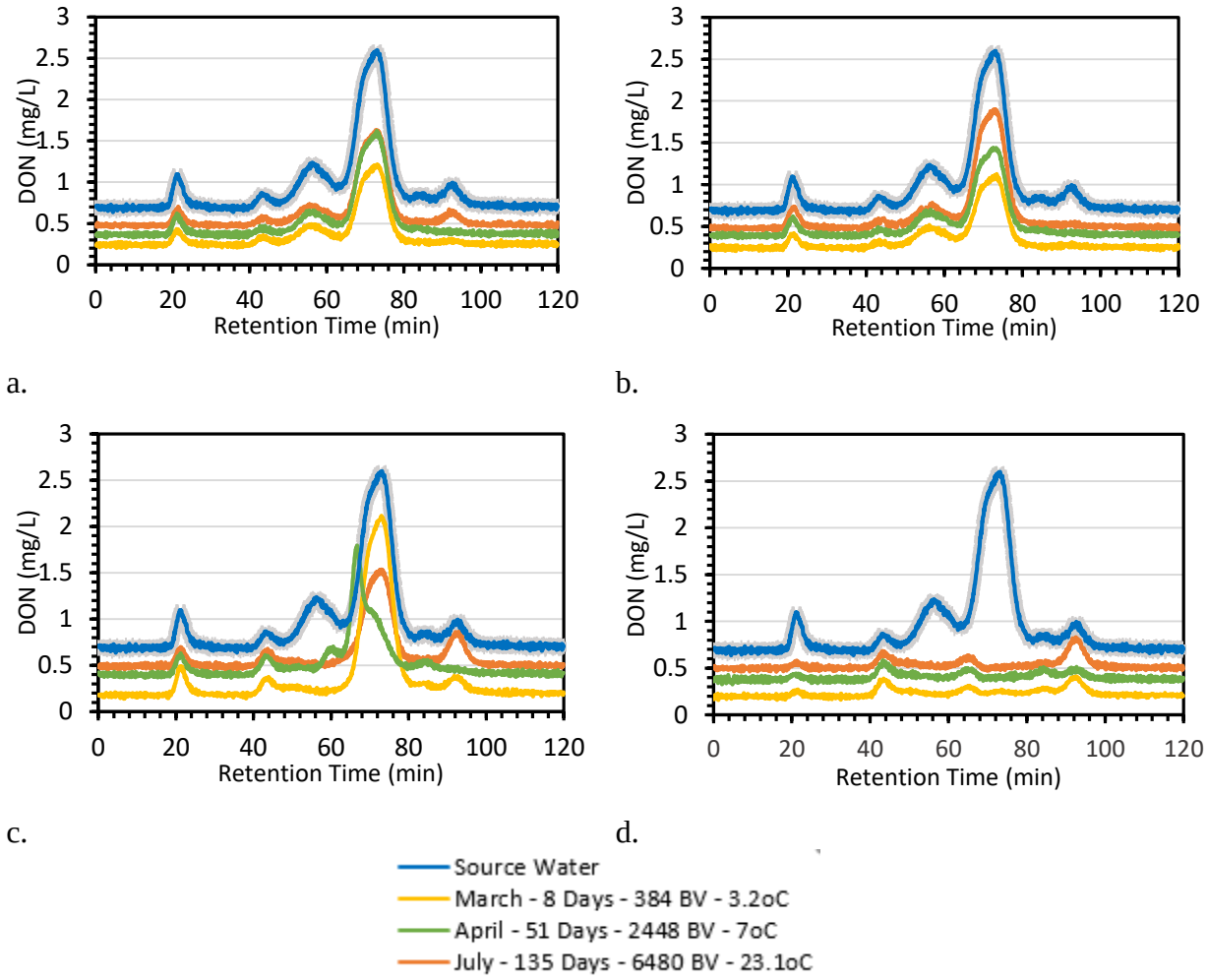

Figure 5.18: Liquid chromatography with organic nitrogen detection (LC-OCD) for (a) GAC, (b) BAC, (c) BIEX and (d) IEX in March, April, July, 2017 – Source water: The average of three source water measurements in March, April and July

5.7. Overall BIEX performance:

The ideal performance of the BIEX is when the DOC effluent meets the treatment objective (<2 mg/L) simultaneous with proper nitrification. In this study, the BIEX filter started operating in the winter at low temperatures (<4°C). Low temperatures are unfavorable for biofilm growth and nitrification. Thus, with increases of DOC because of resin exhaustion and gradual biofilm formation, BIEX eventually began ammonia removal (Figure 5.19).

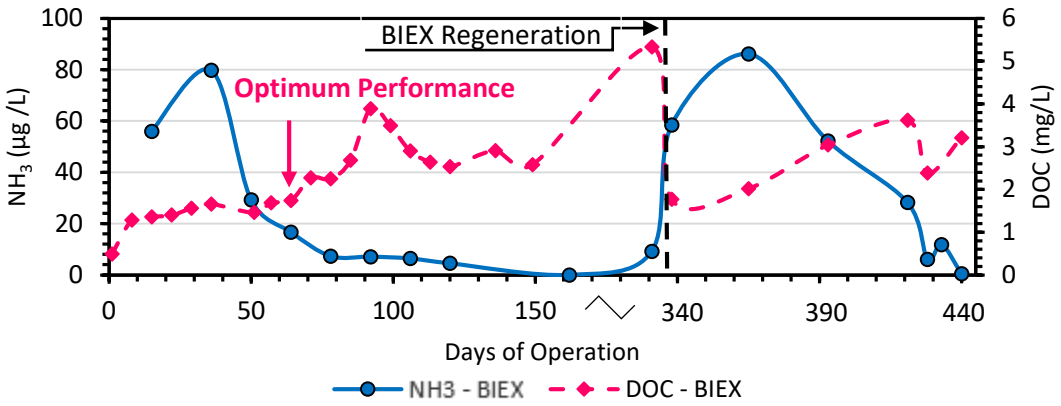

Figure 5.19: BIEX performance: Ammonia removal versus DOC removal

If this project had been started in the summer, the BIEX column might have begun nitrification earlier and nitrification would have been simultaneous with the optimal DOC removal. These results vary based on different source water characteristics and temperature.

CHAPTER 6 GENERAL DISCUSSION

This chapter highlights the main findings of this study. The objective of the current research project was to confirm the viability of operating a BIEX filter for NOM and ammonia removal, when directly fed by colored and turbid surface water. To achieve this goal, we investigated (1) the performance of different media for NOM removal (resins vs. AC); (2) the different modes of operation (sorption on AC, IEX, or biodegradation); (3) the potential nitrification on a BIEX media; (4) the possibility of regenerating BIEX media after long-term operation; and (5) the impact of temperature and turbidity on BIEX performance.

6.1. Performance of different media for NOM removal (resins vs. activated carbon) and modes of operation

With sufficient contact time, IEX filters can remove 30–90% NOM, depending on the water characteristics and resin type (Bolto et al., 2002; Humbert et al., 2005). The weekly regenerated IEX filter in the current study operated in the same range (~80% DOC removal) and retained an effluent DOC concentration below the treatment objective (<2 mg C/L ≈ 1.43 mg C/L). Meanwhile, the BAC filters typically remove 5–20% NOM depending on the source water characteristics, EBCT, and temperature (Terry and Summers, 2017). The BAC filter in the current study operated similarly to those in previous studies (≈4.3% DOC removal). The GAC filter operated similarly to the BAC filter after complete exhaustion (200 days of operation). The BIEX filter behaved similarly to the IEX filter for 52 days of operation and sufficiently removed DOC for 64 days without regeneration (≈1.40 mg C/L, ≈80% DOC removal). The anion exchange capacity measurements along with the effluent DOC concentration and sulfate concentration confirm BIEX filter breakthrough, after which it showed approximately 64% DOC removal in summer. The LC-OCD results suggest that, although 20–50% of aquatic NOM can be biodegraded, roughly 75% of the DOC in the source water in the current study comprises humic substances, a fraction recognized as hardly biodegradable (Catalán et al., 2017). In case of removing NOM, the AEC surpasses the capacity of AC. In addition, high NOM loading on the media, high macroporosity of the resins, and weak electrostatic bonding of NOM to the resin surface probably favor biodegradation activity. Hence, biodegradation may form new sorption sites for additional reactions, as suggested in the concept of bioregeneration (El Gamal et al., 2018). Under such a scenario, the BIEX filter is best described as a process with simultaneous IEX and bioregeneration

mechanisms. In addition, apart from biodegradation after DOC breakthrough, secondary IEX mechanisms (e.g., the displacement of sulfate by NOM) could contribute to the long-term performance of BIEX.

6.2. Possibility to nitrify on BIEX medium

The absence of regeneration for the BIEX filter provided a favorable environment for heterotrophic and nitrifying bacteria growth. Eventually, as the temperature increased and the AEC of the BIEX resin decreased, the microbial growth in the resin beads was sufficient to accomplish complete nitrification (100% ammonia removal). Although the measured biomass on BIEX filter was lower than those for BAC in previous studies (Velten et al., 2007; Zhang et al., 2017), it was close to the biomass measurement on the BAC filter in this study.

6.3. Possibility of BIEX media regeneration after long-term operation

Although it is believed that the accumulation of biomass on IEX resins diminishes the regeneration efficiency, the previous study showed that the BIEX filter was successfully regenerated after 60 days of operation (Winter et al., 2016; Winter et al., 2018). Following that experience, the BIEX filter in current study was regenerated successfully and without complication after 331 days of operation. The AEC and chloride release measurements confirmed that the resin beads were recovered entirely. However, the resin beads were affected by this operation method in terms of their color and size. In addition to the darkening of the resin beads by the growth of biofilm on them, it also decreased the resin bead water content and size. After regeneration, the effluent DOC measurement showed that the BIEX filter resumed performing like the IEX filter and regained its original performance.

It is also worthwhile to mention that, unlike previous suggestions regarding regeneration cycles for IEX filters of 48–72 h, the IEX filter in the current study was regenerated weekly. Although this operation scenario allowed slight colonization of the IEX filter by biomass, the IEX filter performed sufficiently and maintained a constant effluent DOC concentration below the treatment objective.

6.4. Impact of temperature and turbidity on BIEX performance.

The source water showed a large range of turbidity during this project, but the variation showed

no major impact on the filter performances. On the other hand, to determine the effects of temperature on the filters, the activation energies for the IEX, BIEX, and BAC filters were calculated based on the temperature and DOC removal as 20 ± 5, 30 ± 4, and 30 ± 8 kJ/mole, respectively. The higher activation energy of the BIEX filter showed that the BIEX filter was more sensitive to the fluctuation of water temperature than the IEX filter.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

Four parallel pilot filtration columns were fed directly with surface water with a high DOC (~7 mg/L), high turbidity (3–58 NTU), and low mineralization for 442 days. The IEX column, regenerated weekly, presented the highest DOC removal but the lowest ammonia removal. The BIEX filter provided significantly better performance than the BAC filter regarding NOM removal. The BIEX filter exhibited similar nitrification capacities after IEX exhaustion and biofilm growth followed by an increase in temperature to >10°C. The following BIEX performances were noted:

- Effluent DOC concentrations of BIEX were below the treatment goal of ≤2 mg C/L for 64 days (≈ 3072 BV), rose to 4.0 mg C/L after breakthrough, stabilized at 2.5 mg C/L in warm water conditions (3072–6768 BV), and finally increased again to 5.4 mg C/L under winter conditions (<4°C). After 141 days of operation (6768 BV), the BIEX could still decrease TOC from 7.1 to 2.5 mg C/L (October 2017), although its residual AEC was below detection. On the other hand, the BAC filter removed DOC marginally (≈ 7% DOC removal) with the effluent DOC concentration of ~6.7 mg/L.
- The BIEX column began nitrification after 50 days of operation, along with resin exhaustion and the increase of temperature to >7°C. After 162 days of operation (warm water conditions and in biodegradation mode), no trace of ammonia was found in BIEX effluent (100% ammonia removal). Additionally, 111 days after BIEX regeneration, the BIEX filter showed remarkable ammonia removal (98.0%). The BAC filter removed ammonia constantly throughout the study (≈88% ammonia removal).
- After 331 days of operation, the BIEX column was successfully regenerated and the resin capacity was recovered thoroughly. After regeneration, the BIEX filter performed equally to IEX filter.
- The activation energies (temperature effect) calculated after 100 days of operation were 30 ± 4 and 30 ± 8 kJ/mole for the BIEX and BAC filters, respectively. Because of the very low DOC removal by the BAC filter, the activation energy for this medium should be interpreted with caution.
- THM and HAA precursors were significantly lower in the BIEX effluent than in the BAC effluent.

This work inspired the following ideas for future studies. It would be interesting to:

- Investigate BIEX behavior in terms of NOM removal fractions by IEX, adsorption, and biodegradation to gain a better understanding of the removal mechanisms by the BIEX filter;
- Study the correlation of colonization and operational factors;
- Investigate the impact of water resource characteristics on contaminant removal by BIEX in order to properly design an operational plan.

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APPENDICE A

In addition to the data and results presented in chapters 4 and 5, other data in the form of graphs are drawn in the two categories of A. *Operational control* and B. *Insignificant results*.

A. Operational control

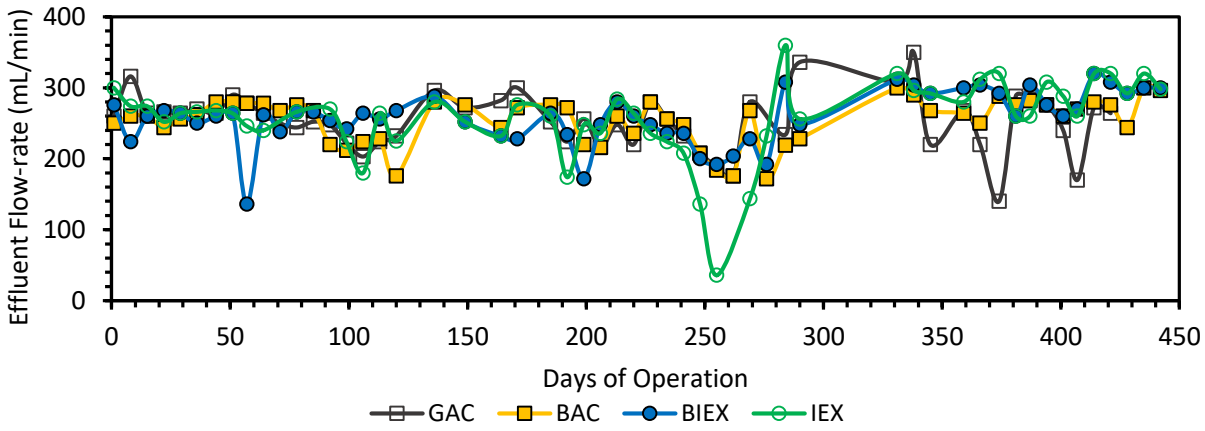


Figure A.1: Weekly effluent flowrate of columns

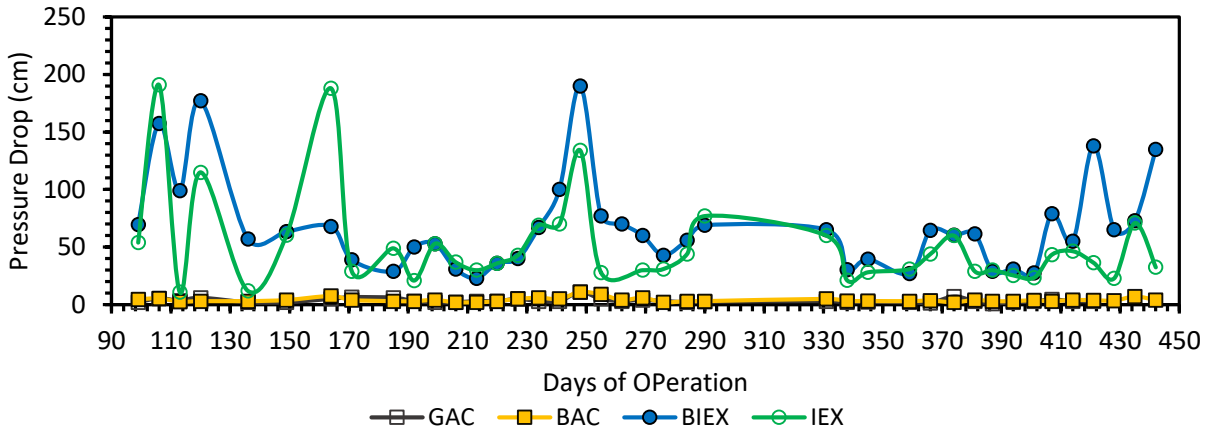


Figure A.2: Controlling pressure drop, starting 90 days after operation

B. Insignificant results

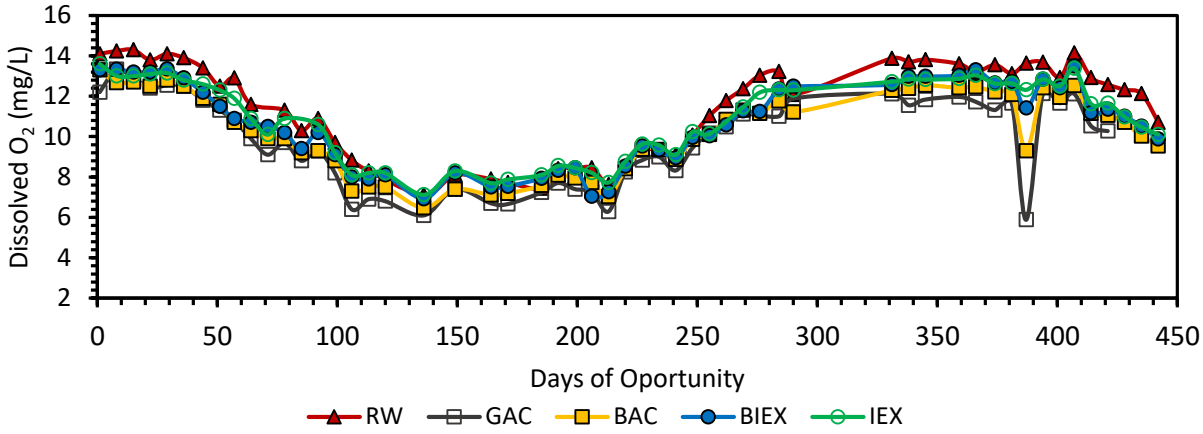


Figure A.3: Dissolved O_2 [mg/L]

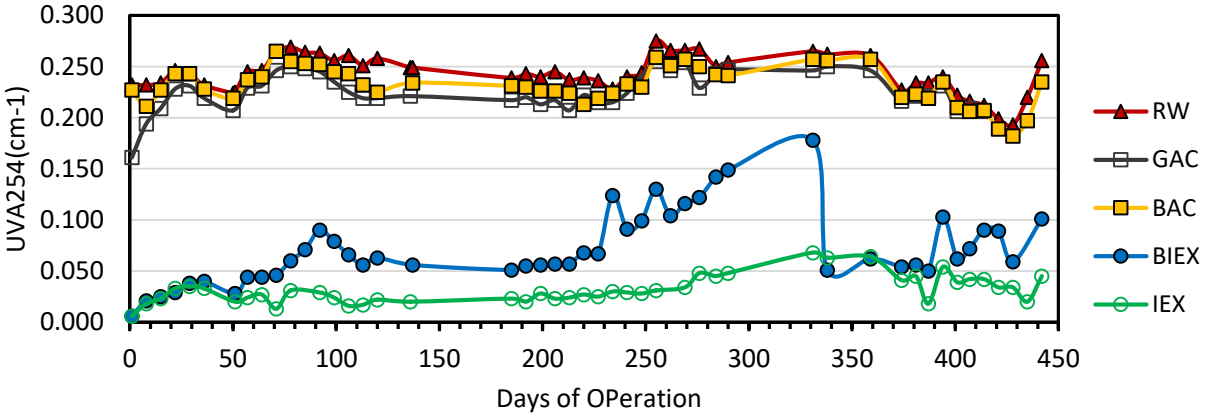


Figure A.4: UV absorbance at 254 nm through time

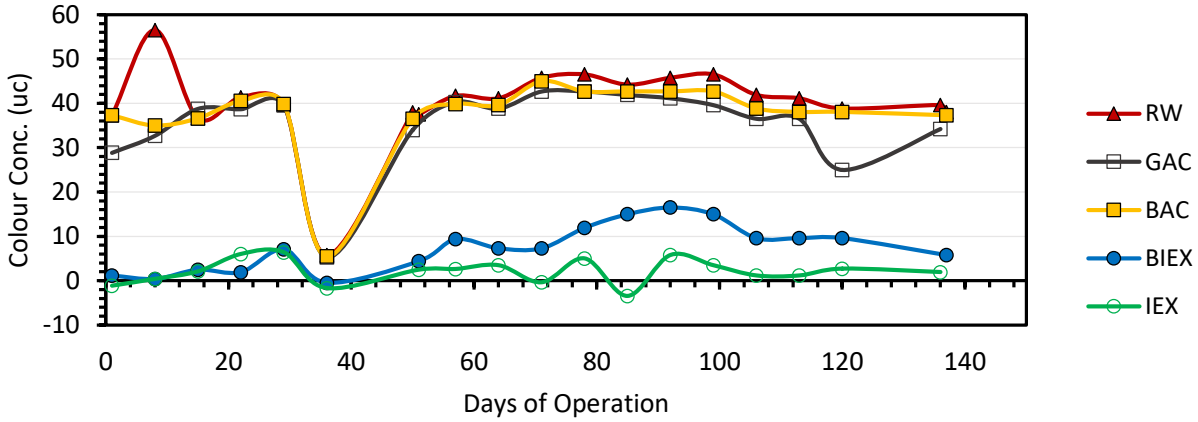


Figure A.5: Colour concentration for 140 days of operation

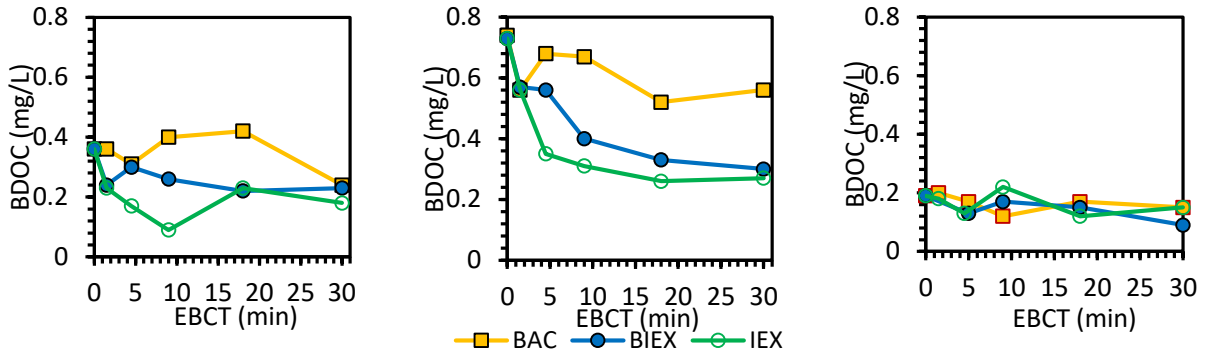


Figure A.6: Impact of EBCT on BDOC removal after, (a) 7 weeks of operation, (b) 19 weeks of operation, (c) 35 weeks of operation

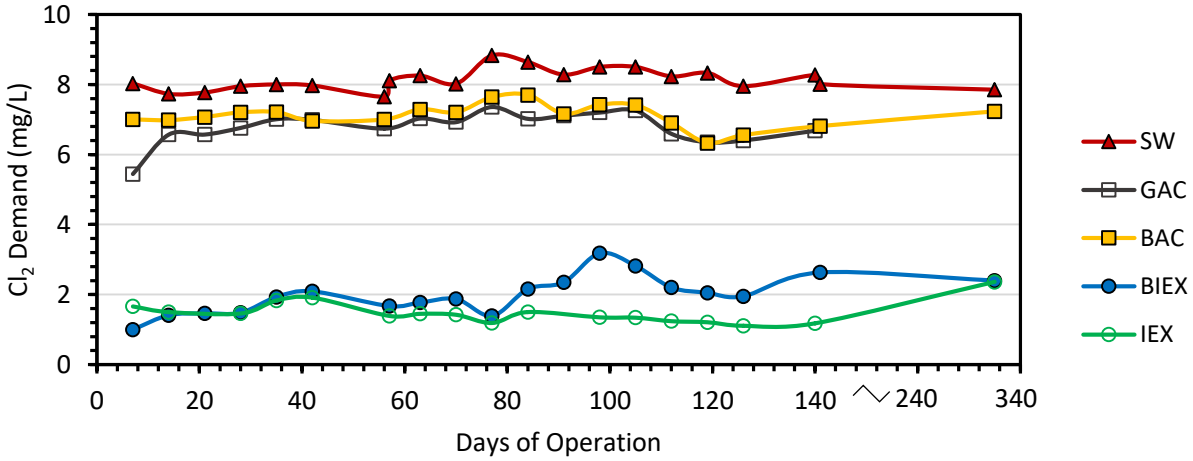


Figure A.7: Cl_2 demand prior to assessing THM-UFC and HAA-UFC concentration

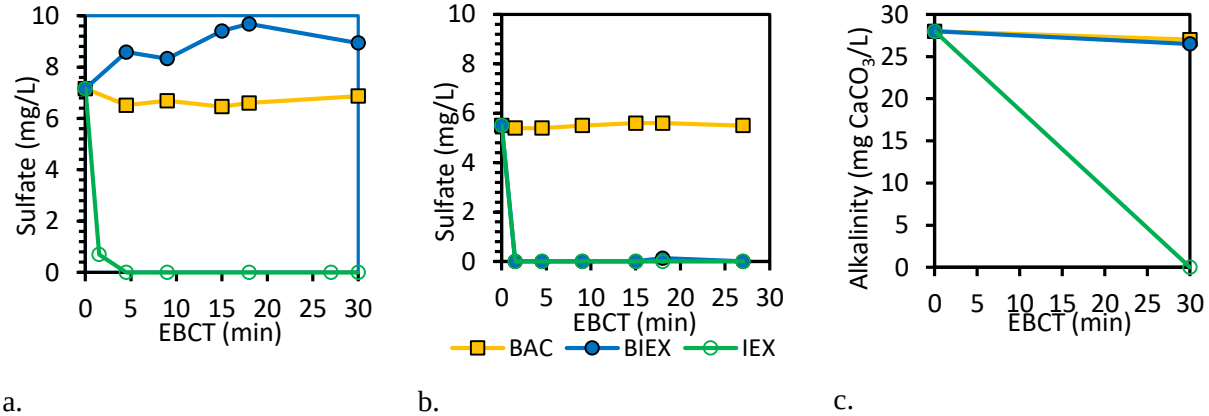
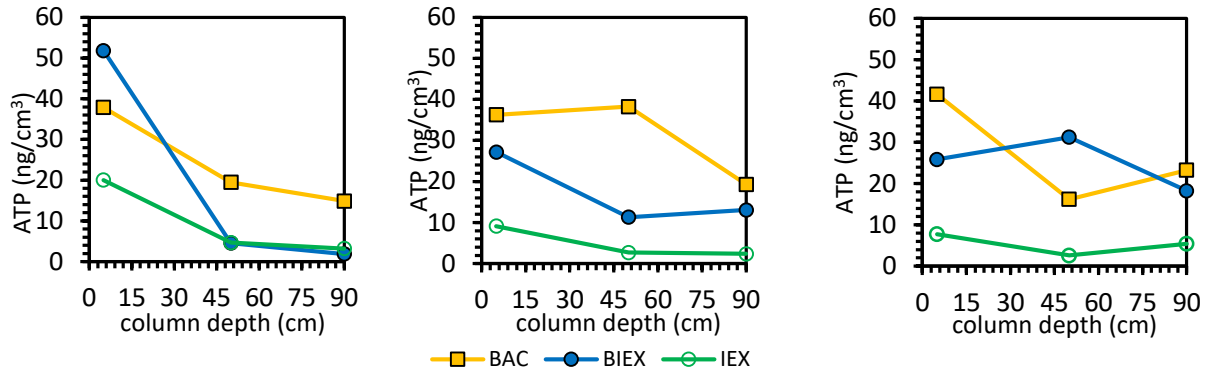
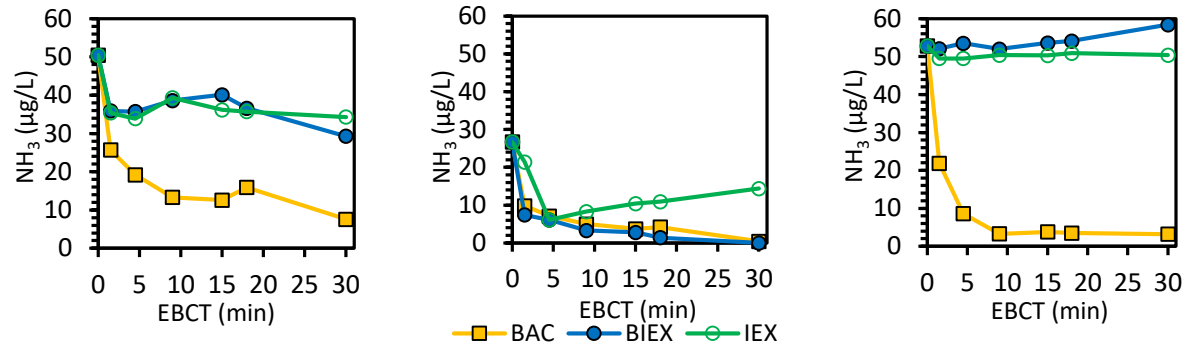


Figure A.8: Impact of EBCT, (a) on sulfate removal after 35 weeks of operation, (b) on sulfate removal after 48 weeks of operation, (c) on alkalinity removal after 35 weeks of operation



a. b. c.

Figure A.9: Impact of column depth on presence of ATP after, (a) 7 weeks of operation, (b) 19 weeks of operation, (c) 48 weeks of operation



a. b. c.

Figure A.10: Impact of EBCT on NH_3 removal after, (a) 7 weeks of operation, (b) 19 weeks of operation, (c) 48 weeks of operation